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(54) Title: FUNCTIONALIZED POLYSTYRENE/POLYDIENE COPOLYMERS AND PROCESSES FOR MAKING SAME

## (57) Abstract

Functionalized polystyrene/polydiene copolymers are prepared with a protected functional organometallic initiator of the formula (II):  $M-R_n-Z-J-[A(R^1R^2R^3)]_x$  wherein M is an alkali metal; R is a saturated or unsaturated hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated diene hydrocarbons, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof; n is an integer from 0 to 5; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; A is an element selected from carbon and silicon; J is oxygen, sulfur, or nitrogen; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, and cycloalkyl and substituted cycloalkyl containing 5 to 12 carbon atoms; and X is dependent on the valence of J and varies from one when J is oxygen or sulfur to two when J is nitrogen, to form a mono-protected, mono-functionalized living copolymer.

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-1-

**FUNCTIONALIZED POLYSTYRENE/POLYDIENE COPOLYMERS  
AND PROCESSES FOR MAKING SAME**

**Cross-Reference to Related Applications**

This application is related to commonly owned  
copending Provisional Application Serial No.  
60/001,842, filed August 3, 1995, and claims the  
5 benefit of its earlier filing date under 35 U.S.C.  
119(e).

**Field of the Invention**

This invention relates to novel  
functionalized copolymers and processes for producing  
10 the same. More particularly, the invention relates  
novel functionalized polystyrene/polydiene copolymers,  
and to processes for the anionic polymerization of  
monomers to produce the same.

**Background of the Invention**

15 Living polymerizations can provide advantages  
over other polymerization techniques, such as well-  
defined polymer structures and low degrees of  
compositional heterogeneity. Many of the variables  
that affect polymer properties can be controlled,  
20 including molecular weight, molecular weight  
distribution, copolymer composition and microstructure,  
stereochemistry, branching and chain end functionality.

Living anionic polymerization of styrene and  
diene monomers was first described by Szwarc and his  
25 coworkers. See M. Szwarc, *Nature* 178, 1169 (1956) and  
M. Szwarc, et al., *J.Am.Chem.Soc.* 78, 2656 (1956).

-2-

Many useful materials can be prepared by anionically polymerizing olefinic-containing monomers, such as styrene and dienes, in the presence of an organo-alkali metal initiator. For example, conventionally,

5 conjugated dienes and styrene monomers are anionically polymerized using lithium initiators, such as sec- and tert-butyllithium. The resultant polymer, which has an active alkali metal end group, can thereafter be reacted with a reagent which will couple the polymer  
10 molecules or replace the alkali metal with a functional group.

While alkyllithium initiators can be useful to prepare mono-functional polymers, di-functional, or telechelic, polymers cannot be produced using these  
15 initiators. Telechelic polymers are polymers that contain two functional groups per molecule at the termini of the polymer. Such polymers have found wide utility in many applications. For instance, telechelic polymers have been employed as rocket fuel binders, in  
20 coatings and sealants and in adhesives. In addition, polymers that contain two hydroxyl groups per molecule can be co-polymerized with appropriate materials to form segmented polyesters, polyurethanes, polycarbonates, and polyamides (see U.S. Patent No.  
25 4,994,526).

A variety of polymerization techniques, such as cationic and free radical polymerizations, have been employed to prepare telechelic polymers. However, functionality can be best controlled with anionic  
30 polymerization. An early approach to the preparation of telechelic polymers is described in D.N. Schulz, et al, *J. Polym. Sci., Polym. Chem. Ed.* 12, 153 (1974), which describes the reaction of a hydroxy protected initiator with butadiene. The resultant living anion  
35 was quenched with ethylene oxide to afford mono-protected di-hydroxy polybutadiene. While excellent functionality ( $f = 1.87-2.02$ ) was achieved by

- 3 -

this process, the protected initiator was insoluble in hydrocarbon solution. Therefore, the reaction was conducted in diethyl ether, and as a result, relatively high 1,2 microstructure (31-54%) was obtained.

5           Another approach that has been employed to prepare telechelic polymers is the generation and subsequent functionalization of a "dilithium initiator". A dilithium initiator is typically prepared by the addition of two equivalents of  
10 secondary butyllithium to *meta*-diisopropenylbenzene. The dilithium initiator is then reacted with a conjugated diene, such as butadiene or isoprene, to form a polymer chain with two anionic sites. The resultant polymer chain is then reacted with two  
15 equivalents of a functionalizing agent, such as ethylene oxide. While useful, gelation is frequently observed during the functionalization step. This leads to lower capping efficiency (see, for example, U.S. Patent No. 5,393,843, Example 1, wherein the capping  
20 efficiency was only 82%). Additional details of this gelation phenomenon are described in U.S. Patent No. 5,478,899. Further, this dilithium approach can only afford telechelic polymers with the same functional group on each end of the polymer chain.

25           Great Britain published patent application 2,241,239, published August 28, 1991, describes a novel approach for producing telechelic polymers in hydrocarbon solution. Telechelic polymers were prepared using monofunctional silyl ether initiators  
30 containing alkali metal end groups that were soluble in hydrocarbon solutions. These monofunctional silyl ether initiators were demonstrated to be useful in producing dihydroxy (telechelic) polybutadienes having desirable characteristics, such as a molecular weight  
35 of typically 1,000 to 10,000, a 1,4 microstructure content of typically 90%, and the like.

- 4 -

Summary of the Invention

The present invention provides novel alkenylsubstituted aromatic/polydiene copolymers, preferably polystyrene/polyisoprene or polybutadiene  
5 copolymers, including functionalized, telechelic, hetero-telechelic, and multi-branched and star copolymers thereof, and processes for preparing the same. The copolymers can be block, tapered or random copolymers. The novel copolymers of the invention can  
10 have good functionalization, from about one for mono-functional copolymers, and about 2 for telechelic copolymers. The novel copolymers of the invention have applications in a variety of areas, and are particularly useful as viscosity modifiers for  
15 lubricants, for example, a viscosity index improving additive having a "built-in" compatibilizing functional group having dispersant properties for motor oils.

The present invention also provides processes for anionic copolymerization of alkenylsubstituted  
20 aromatic hydrocarbon and diene monomers to produce the copolymers of the invention. The copolymers of the invention are prepared using protected functionalized initiators. Block copolymers can be provided by sequentially reacting monomers selected from conjugated  
25 diene hydrocarbons and alkenylsubstituted aromatic hydrocarbons. Tapered copolymers can be prepared by reacting a mixture of monomers selected from conjugated diene hydrocarbons and alkenylsubstituted aromatic hydrocarbons. Still further, random copolymers can be  
30 prepared by reacting a mixture of monomers selected from conjugated diene hydrocarbons and alkenylsubstituted aromatic hydrocarbons, in the presence of a polar modifier.

The resultant living copolymer can be  
35 quenched, for example with acidic methanol, to afford a protected copolymer with a functional group at the

-5-

initiating chain end thereof. Removal of the protecting group results in a functionalized copolymer.

Alternatively, the resultant living copolymer can be quenched with various functionalizing agents, such as ethylene oxide, carbon dioxide, epichlorohydrin, and the like, to afford a mono-protected telechelic copolymer. The functional groups on the termini of the polymer can be the same (such as two hydroxyl groups) or different (such as one hydroxyl group and one amino group). The copolymers can optionally be hydrogenated to remove aliphatic unsaturations. The protecting group can also be removed to provide telechelic or heterotelechelic copolymers, either before or after the optional hydrogenation.

Protected, functionalized star polymers can also be prepared by coupling the living polymer with known coupling agents such as silicon tetrachloride, tin tetrachloride, isomers of divinylbenzene, and the like. Subsequent deprotection affords functionalized stars.

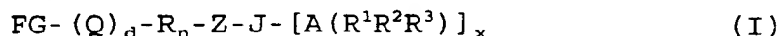
In contrast to star polymers of the prior art, the molecular architecture of compounds of the present invention can be precisely controlled. For example, each arm of the multi-arm polymer can contain a functional group (protected or non-protected), and the functional groups (and/or protecting groups) can be the same or different, through use of mixtures of initiators with different protected functionalities to initiate polymerization. The star polymers can also include both functional and non-functional ends by using combinations of protected functional initiators and alkylolithium initiators to initiate polymerization. The nature of the functional group and/or protecting group and/or non-functional group can be varied simply by changing the initiator, and the ratio of one functional group to another functional group, or of one functional group to a non-functional group, can be

-6-

adjusted by simply varying the ratio of initiators to one another. Further, monomer identity, monomer composition and molecular weight of both functional and non-functional arms can be independently manipulated by  
5 varying the monomer charged by each initiator. Still further, the number of polymer arms can be adjusted by varying the nature of the coupling agent, and the ratio of living polymer to the coupling agent.

### Detailed Description of the Invention

10 The copolymers of the present invention can be represented generally by following formula:



wherein:

15 FG is H or a protected or non-protected functional group;

Q is a saturated or unsaturated hydrocarbyl group derived by incorporation of a conjugated diene hydrocarbon and an alkenylsubstituted aromatic hydrocarbon, sequentially or as a mixture thereof;

20 d is an integer from 10 to 4000;

R is a saturated or unsaturated hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated diene hydrocarbons, alkenylsubstituted aromatic hydrocarbons,  
25 and mixtures thereof;

n is an integer from 0 to 5;

Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups;

30 J is oxygen, sulfur, or nitrogen;

$[\text{A}(\text{R}^1\text{R}^2\text{R}^3)]_x$  is a protecting group, wherein

A is an element selected from Group IVa of the Periodic Table of Elements;

35  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower



-7-

alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, and cycloalkyl and substituted cycloalkyl containing 5 to 12 carbon atoms; and

x is dependent on the valence of J and varies from one when J is oxygen or sulfur to two when J is nitrogen.

#### Removal of the protecting group

(deprotection) produces polymers with oxygen, sulfur or nitrogen functional groups on the ends of the polymers. The residual aliphatic unsaturation can be optionally removed by hydrogenation before or after removal of the protecting groups. These functional groups can then participate in various copolymerization reactions by reaction of the functional groups on the ends of the polymer with selected difunctional or polyfunctional comonomers and/or linking or coupling agents, as described in more detail below.

The alkenylsubstituted aromatic hydrocarbon and conjugated diene to be anionically copolymerized are chosen from the group of unsaturated organic compounds that can be polymerized anionically (i.e. in a reaction initiated by an organo-alkali metal).

Examples of polymerizable alkenylsubstituted aromatic hydrocarbons include, but are not limited to, styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinyl-naphthalene, 2-alpha-

methylvinyl-naphthalene, 1,2-diphenyl-4-methyl-1-hexene and mixtures of these, as well as alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl derivatives thereof in which the total number of carbon atoms in the combined hydrocarbon constituents is generally not greater than

18. Examples of these latter compounds include 3-methylstyrene, 3,5-diethylstyrene, 4-tert-butylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-p-

- 8 -

tolylstyrene, 2,4-divinytoluene and 4,5-dimethyl-1-vinylnaphthalene. U.S. Patent No. 3,377,404, incorporated herein by reference in its entirety, discloses suitable additional alkenylsubstituted aromatic compounds.

The conjugated diene is preferably a 1,3-diene. Examples of suitable conjugated diene hydrocarbons include, but are not limited to, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, and 2-methyl-3-isopropyl-1,3-butadiene.

The copolymers of the present invention can be prepared by the sequential reaction of conjugated alkadienes and alkenylsubstituted aromatic hydrocarbons with protected functional organolithium initiators to form a mono-protected mono-functional living block copolymer. Alternatively, novel copolymers of the invention can be prepared by the reaction of the protected functional organolithium initiator with a mixture of conjugated alkadienes and alkenylsubstituted aromatic hydrocarbons to form a mono-protected mono-functional living tapered or random copolymer.

The mono-protected mono-functional living copolymer can be quenched or terminated by addition of a suitable proton donor, such as water, methanol, isopropanol, acetic acid, and the like, to provide a mono-functional copolymer. Alternatively, polymerization can be followed by functionalization of the resultant living anion with a suitable electrophile to provide a mono-protected, di-functional polymer. The di-functional copolymer may be telechelic, i.e., contain two functional groups, which are the same, per

-9-

molecule at the termini of the polymer. The copolymer can also be hetero-telechelic, having different functionalities at opposite ends of the polymer chain. This is represented schematically by the formula

5 A-----B, wherein A and B are different functional groups.

A telechelic di-protected di-functional copolymer having random, tapered or sequential blocks can be formed by reacting the living copolymer with a

10 difunctional linking agent, such as ethylbenzoate, xylene dibromide or dimethyldichlorosilane. In the case of the sequential or tapered block copolymer, this linking reaction will result in a telechelic difunctional triblock copolymer, with di-protected di-

15 functionality.

The product polymer can be hydrogenated, either before or after removing the protecting group.

Electrophiles that are useful in functionalizing the polymeric living copolymer include,

20 but are not limited to, alkylene oxides, such as ethylene oxide, propylene oxide, styrene oxide, and oxetane; oxygen; sulfur; carbon dioxide; halogens such as chlorine, bromine and iodine; haloalkyltrialkoxysilanes, alkenylhalosilanes, and

25 omega-alkenylarylhalosilanes, such as chlorotrimethylsilane and styrenyldimethyl chlorosilane; sulfonated compounds, such as 1,3-propane sultone; amides, including cyclic amides, such as caprolactam, N-benzylidene trimethylsilylamide, and

30 dimethyl formamide; silicon acetals; 1,5-diazabicyclo[3.1.0]hexane; allyl halides, such as allyl bromide and allyl chloride; methacryloyl chloride; amines, including primary, secondary, tertiary and cyclic amines, such as 3-(dimethylamino)-propyl

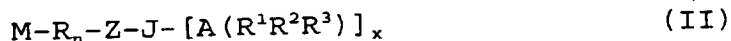
35 chloride and N-(benzylidene)trimethylsilylamine; epihalohydrins, such as epichlorohydrin, epibromohydrin, and epiiodohydrin, and other materials

-10-

as known in the art to be useful for terminating or end capping polymers. These and other useful functionalizing agents are described, for example, in U.S. Patent Nos. 3,786,116 and 4,409,357, the entire disclosure of each of which is incorporated herein by reference. As noted above, the copolymer optionally is hydrogenated, either before after removal of the protecting group.

Exemplary organolithium initiators useful in the present invention include initiators selected from the group consisting of omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, omega-(tert-butyldimethylsilyloxy)-1-alkyllithiums, omega-(tert-butyldimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums.

Initiators useful (II) in the preparation of polymers of the present invention are also represented by the following formula:

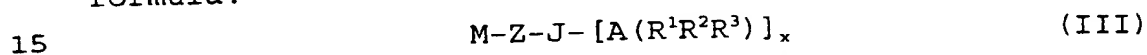


wherein M is an alkali metal, R is a saturated or unsaturated hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated diene hydrocarbons, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof; n is an integer from 0 to 5; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups;

-11-

J is a hetero atom, e.g., oxygen, sulfur, or nitrogen;  
A is an element selected from Group IVa of the Periodic  
Table of Elements; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently  
selected from hydrogen, alkyl, substituted alkyl groups  
5 containing lower alkyl, lower alkylthio, and lower  
dialkylamino groups, aryl or substituted aryl groups  
containing lower alkyl, lower alkylthio, and lower  
dialkylamino groups, and cycloalkyl and substituted  
cycloalkyl containing 5 to 12 carbon atoms; and x is  
10 dependent on the valence of J and varies from one when  
J is oxygen or sulfur to two when J is nitrogen.

These initiators can be prepared by reaction  
of protected organolithium compounds of the following  
formula:



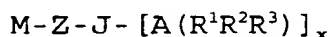
wherein each of M, Z, J, A, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and x are the  
same as defined above, with conjugated alkadienes (such  
as butadiene or isoprene), alkenylsubstituted aromatic  
hydrocarbons (such as styrene or alpha-methylstyrene),  
20 and mixtures thereof, to form an extended hydrocarbon  
chain between M and Z in Formula (III), which extended  
chain is denoted as R<sub>n</sub> in Formula (II).

The compounds of Formula (III) can be  
prepared by first reacting in an inert solvent a  
25 selected tertiary amino-1-haloalkane, omega-hydroxy-  
protected-1-haloalkane or omega-thio-protected-1-  
haloalkane, depending on whether J is to be N, O or S,  
(the alkyl portions of the haloalkyl groups contain 3  
to 25 carbon atoms) with an alkali metal, preferably  
30 lithium, at a temperature between about 35°C and about  
130°C, preferably at the solvent reflux temperature, to  
form a protected monofunctional alkali metal initiator  
(of Formula III), which is then optionally reacted with  
a one or more conjugated diene hydrocarbons, one or  
35 more alkenylsubstituted aromatic hydrocarbons, or  
mixtures of one or more dienes with one or more  
alkenylsubstituted aromatic hydrocarbons, in a

-12-

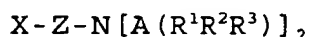
predominantly alkane, cycloalkane, or aromatic reaction solvent, which solvent contains 5 to 10 carbon atoms, and mixtures of such solvents to produce a monofunctional initiator with an extended chain or  
5 tether between the metal atom (M) and element (J) in Formula (II) above and mixtures thereof with compounds of Formula (III). R in Formula (II) is preferably derived from conjugated 1,3-dienes. While A in the protecting group  $[A(R^1R^2R^3)]$  of the formulae above can  
10 be any of the elements in Group IVa of the Periodic Table of the Elements, carbon and silicon currently appear the most useful, especially when polymerizing conjugated dienes.

Incorporation of R groups into the M-Z  
15 linkage to form the compounds of Formula (II) above involves addition of compounds of the Formula



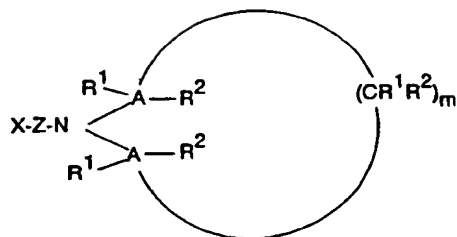
where the symbols have the meanings ascribed above, across the carbon to carbon double bonds in compounds  
20 selected from the consisting of one or more conjugated diene hydrocarbons, one or more alkenylsubstituted aromatic hydrocarbons, or mixtures of one or more dienes with one or more alkenylsubstituted aromatic hydrocarbons, to produce new carbon-lithium bonds of an  
25 allylic or benzylic nature, much like those found in a propagating polyalkadiene or polyarylethylene polymer chain derived by anionic initiation of the polymerization of conjugated dienes or arylethylenes. These new carbon-lithium bonds are now activated toward  
30 polymerization and so are much more efficient in promoting polymerization than the precursor M-Z (M=Li) bonds, themselves.

Tertiary amino-1-haloalkanes useful in practicing this invention include compounds of the  
35 following general structures:



and

- 13 -



wherein X is halogen, preferably chlorine or bromine; Z is a branched or straight chain hydrocarbon tether or connecting group which contains 3-25 carbon atoms, which tether may also contain aryl or substituted aryl groups; A is an element selected from Group IVa of the Periodic Table of the Elements; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently defined as hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms; and m is an integer from 1 to 7, and their employment as initiators in the anionic polymerization of olefin containing monomers in an inert, hydrocarbon solvent optionally containing a Lewis base. The process reacts selected tertiary amino-1-haloalkanes whose alkyl groups contain 3 to 25 carbon atoms, with alkali metal, preferably lithium, at a temperature between about 35°C and about 130°C, preferably at the reflux temperature of an alkane, cycloalkane or aromatic reaction solvent containing 5 to 10 carbon atoms and mixtures of such solvents.

25                   Anionic polymerizations employing the  
tertiary amine initiators are conducted in an inert  
solvent, preferably a non-polar solvent, optionally  
containing an ethereal modifier, using an olefinic  
monomer which is an alkenylsubstituted aromatic  
30 hydrocarbon or a 1,3-diene at a temperature of about -

-14-

30°C to about 150°C. The polymerization reaction proceeds from initiation to propagation and is finally terminated with appropriate reagents so that the polymer is mono-functionally or di-functionally  
5 terminated. The polymers may have a molecular weight range of about 1000 to 50,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

Tertiary amino-1-haloalkanes useful in the  
10 practice of this invention include, but are not limited to, 3-(N,N-dimethylamino)-1-propyl halide, 3-(N,N-dimethylamino)-2-methyl-1-propyl halide, 3-(N,N-dimethylamino)-2,2-dimethyl-1-propyl halide, 4-(N,N-dimethylamino)-1-butyl halide, 5-(N,N-dimethylamino)-1-  
15 pentyl halide, 6-(N,N-dimethylamino)-1-hexyl halide, 3-(N,N-diethylamino)-1-propyl halide, 3-(N,N-diethylamino)-2-methyl-1-propyl halide, 3-(N,N-diethylamino)-2,2-dimethyl-1-propyl halide, 4-(N,N-diethylamino)-1-butyl halide, 5-(N,N-diethylamino)-1-  
20 pentyl halide, 6-(N,N-diethylamino)-1-hexyl halide, 3-(N-ethyl-N-methylamino)-1-propyl halide, 3-(N-ethyl-N-methylamino)-2-methyl-1-propyl halide, 3-(N-ethyl-N-methylamino)-2,2-dimethyl-1-propyl halide, 4-(N-ethyl-N-methylamino)-1-butyl halide, 5-(N-ethyl-N-  
25 methylamino)-1-pentyl halide, 6-(N-ethyl-N-methylamino)-1-hexyl halide, 3-(piperidino)-1-propyl halide, 3-(piperidino)-2-methyl-1-propyl halide, 3-(piperidino)-2,2-dimethyl-1-propyl halide, 4-(piperidino)-1-butyl halide, 5-(piperidino)-1-pentyl  
30 halide, 6-(piperidino)-1-hexyl halide, 3-(pyrrolidino)-1-propyl halide, 3-(pyrrolidino)-2-methyl-1-propyl halide, 3-(pyrrolidino)-2,2-dimethyl-1-propyl halide, 4-(pyrrolidino)-1-butyl halide, 5-(pyrrolidino)-1-pentyl halide, 6-(pyrrolidino)-1-hexyl halide, 3-  
35 (hexamethyleneimino)-1-propyl halide, 3-(hexamethyleneimino)-2-methyl-1-propyl halide, 3-(hexamethyleneimino)-2,2-dimethyl-1-propyl halide, 4-



-15-

(hexamethyleneimino)-1-butyl halide, 5-  
(hexamethyleneimino)-1-pentyl halide, 6-  
(hexamethyleneimino)-1-hexyl halide, 3-(N-isopropyl-N-methyl)-1-propyl halide, 2-(N-isopropyl-N-methyl)-2-methyl-1-propyl halide, 3-(N-isopropyl-N-methyl)-2,2-dimethyl-1-propyl halide, and 4-(N-isopropyl-N-methyl)-1-butyl halide. The halo- or halide group is preferably selected from chlorine and bromine.

Omega-hydroxy-protected-1-haloalkanes useful  
10 in producing monofunctional ether initiators useful in practicing this invention have the following general structure:



wherein X is halogen, preferably chlorine or bromine; Z  
15 is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; and  $R^1$ ,  $R^2$ , and  $R^3$  are independently defined as hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio,  
20 and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms, and their employment as initiators in the  
25 anionic polymerization of olefin containing monomers in an inert, hydrocarbon solvent optionally containing a Lewis base. The process reacts selected omega-hydroxy-protected-1-haloalkanes whose alkyl groups contain 3 to 25 carbon atoms, with alkali metal, preferably lithium,  
30 at a temperature between about 35°C and about 130°C, preferably at the reflux temperature of an alkane, cycloalkane or aromatic reaction solvent containing 5 to 10 carbon atoms and mixtures of such solvents.

Anionic polymerizations employing the  
35 monofunctional ether initiators are conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal modifier, using an

-16-

olefinic monomer which is an alkenylsubstituted aromatic hydrocarbon or a 1,3-diene at a temperature of about -30°C to about 150°C. The polymerization reaction proceeds from initiation to propagation and is finally terminated with appropriate reagents so that the polymer is mono-functionally or di-functionally terminated. The polymers may have a molecular weight range of about 1000 to 50,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

The precursor omega-protected-1-haloalkanes (halides) can be prepared from the corresponding haloalcohol by standard literature methods. For example, 3-(1,1-dimethylethoxy)-1-chloropropane can be synthesized by the reaction of 3-chloro-1-propanol with 2-methylpropene according to the method of A. Alexakis, M. Gardette, and S. Colin, Tetrahedron Letters, 29, 1988, 2951. The method of B. Figadere, X. Franck and A. Cave, Tetrahedron Letters, 34, 1993, 5893, which involves the reaction of the appropriate alcohol with 2-methyl-2-butene catalyzed by boron trifluoride etherate, can be employed for the preparation of the t-amyl ethers. The alkoxy, alkylthio or dialkylamino substituted ethers, for example 6-[3-(methylthio)-1-propyloxy]-1-chlorohexane, can be synthesized by reaction of the corresponding substituted alcohol, for instance 3-methylthio-1-propanol, with an alpha-bromo-omega-chloroalkane, for instance 1-bromo-6-hexane, according to the method of J. Almena, F. Foubelo and M. Yus, Tetrahedron, 51, 1995, 11883. The compound 4-(methoxy)-1-chlorobutane, and the higher analogs, can be synthesized by the ring opening reaction of tetrahydrofuran with thionyl chloride and methanol, according to the procedure of T. Ferrari and P. Vogel, SYNLETT, 1991, 233. The triphenylmethyl protected compounds, for example 3-(triphenylmethoxy)-1-chloropropane, can be prepared by the reaction of the

-17-

haloalcohol with triphenylmethylchloride, according to the method of S. K. Chaudhary and O. Hernandez, Tetrahedron Letters, 1979, 95.

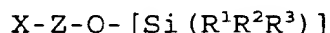
Omega-hydroxy-protected-1-haloalkanes

- 5 prepared in accordance with this earlier process useful in practicing this invention include, but are not limited to, 3-(1,1-dimethylethoxy)-1-propyl halide, 3-(1,1-dimethylethoxy)-2-methyl-1-propyl halide, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyl halide, 4-(1,1-dimethylethoxy)-1-butyl halide, 5-(1,1-dimethylethoxy)-1-pentyl halide, 6-(1,1-dimethylethoxy)-1-hexyl halide, 8-(1,1-dimethylethoxy)-1-octyl halide, 3-(1,1-dimethylpropoxy)-1-propyl halide, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyl halide, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyl halide, 4-(1,1-dimethylpropoxy)-1-butyl halide, 5-(1,1-dimethylpropoxy)-1-pentyl halide, 6-(1,1-dimethylpropoxy)-1-hexyl halide, 8-(1,1-dimethylpropoxy)-1-octyl halide, 4-(methoxy)-1-butyl halide, 4-(ethoxy)-1-butyl halide, 4-(propyloxy)-1-butyl halide, 4-(1-methylethoxy)-1-butyl halide, 3-(triphenylmethoxy)-2,2-dimethyl-1-propyl halide, 4-(triphenylmethoxy)-1-butyl halide, 3-[3-(dimethylamino)-1-propyloxy]-1-propyl halide, 3-[2-(dimethylamino)-1-ethoxy]-1-propyl halide, 3-[2-(diethylamino)-1-ethoxy]-1-propyl halide, 3-[2-(diisopropylamino)-1-ethoxy]-1-propyl halide, 3-[2-(1-piperidino)-1-ethoxy]-1-propyl halide, 3-[2-(1-pyrrolidino)-1-ethoxy]-1-propyl halide, 4-[3-(dimethylamino)-1-propyloxy]-1-butyl halide, 6-[2-(1-piperidino)-1-ethoxy]-1-hexyl halide, 3-[2-(methoxy)-1-ethoxy]-1-propyl halide, 3-[2-(ethoxy)-1-ethoxy]-1-propyl halide, 4-[2-(methoxy)-1-ethoxy]-1-butyl halide, 5-[2-(ethoxy)-1-ethoxy]-1-pentyl halide, 3-[3-(methylthio)-1-propyloxy]-1-propyl halide, 3-[4-(methylthio)-1-butyloxy]-1-propyl halide, 3-(methylthiomethoxy)-1-propyl halide, 6-[3-(methylthio)-

-18-

1-propyloxy]-1-hexyl halide, 3-[4-(methoxy)-benzyloxy]-  
1-propyl halide, 3-[4-(1,1-dimethylethoxy)-benzyloxy]-  
1-propyl halide, 3-[2,4-(dimethoxy)-benzyloxy]-1-propyl  
halide, 8-[4-(methoxy)-benzyloxy]-1-octyl halide, 4-[4-  
5 (methylthio)-benzyloxy]-1-butyl halide, 3-[4-  
(dimethylamino)-benzyloxy]-1-propyl halide, 6-[4-  
(dimethylamino)-benzyloxy]-1-hexyl halide, 5-  
(triphenylmethoxy)-1-pentyl halide, 6-  
(triphenylmethoxy)-1-hexyl halide, and 8-  
10 (triphenylmethoxy)-1-octyl halide. The halo- or halide  
group is preferably selected from chlorine and bromine.

U.S. Patent 5,362,699 discloses a process for  
the preparation of hydrocarbon solutions of  
monofunctional ether initiators derived from omega-  
15 hydroxy-silyl-protected-1-haloalkanes of the following  
general structure:



wherein X is halogen, preferably chlorine or bromine; Z  
is a branched or straight chain hydrocarbon group which  
20 contains 3-25 carbon atoms, optionally containing aryl  
or substituted aryl groups; and R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are  
independently defined as saturated and unsaturated  
aliphatic and aromatic radicals, and their employment  
as initiators in the anionic polymerization of olefin  
25 containing monomers in an inert, hydrocarbon solvent  
optionally containing a Lewis base. The process reacts  
selected omega-hydroxy-protected-1-haloalkanes whose  
alkyl groups contain 3 to 25 carbon atoms, with lithium  
metal at a temperature between about 25°C and about  
30 40°C, in an alkane or cycloalkane reaction solvent  
containing 5 to 10 carbon atoms and mixtures of such  
solvents.

Anionic polymerizations employing the  
monofunctional siloxy ether initiators are conducted in  
35 an inert solvent, preferably a non-polar solvent,  
optionally containing an ethereal modifier, using an  
olefinic monomer which is an alkenylsubstituted

-19-

aromatic hydrocarbon or a 1,3-diene at a temperature of about -30°C to about 150°C. The polymerization reaction proceeds from initiation to propagation and is finally terminated with appropriate reagents so that the polymer is mono-functionally or di-functionally terminated. The polymers may have a molecular weight range of about 1000 to 50,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

10           Omega-silyl-protected-1-haloalkanes prepared in accordance with this earlier process useful in practicing this invention include, but are not limited to, 3-(t-butyldimethylsilyloxy)-1-propyl halide, 3-(t-butyldimethylsilyloxy)-2-methyl-1-propyl halide, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyl halide, 4-(t-butyldimethylsilyloxy)-1-butyl halide, 5-(t-butyldimethylsilyloxy)-1-pentyl halide, 6-(t-butyldimethylsilyloxy)-1-hexyl halide, 8-(t-butyldimethylsilyloxy)-1-octyl halide, 3-(t-butyldiphenylsilyloxy)-1-propyl halide, 3-(t-butyldiphenylsilyloxy)-2-methyl-1-propyl halide, 3-(t-butyldiphenylsilyloxy)-2,2-dimethyl-1-propyl halide, 4-(t-butyldiphenylsilyloxy)-1-butyl halide, 6-(t-butyldiphenylsilyloxy)-1-hexyl halide and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyl halide. The halo- or halide group is preferably selected from chlorine and bromine.

Monofunctional thioether initiators useful in the practice of this invention can be derived from omega-thio-protected-1-haloalkanes of the following general structure:



wherein X is halogen, preferably chlorine or bromine; Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups; [A(R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>)] is a protecting group in which A is an element selected from Group IVA

-20-

of the Periodic Table of the Elements; and  $R^1$ ,  $R^2$ , and  $R^3$  are independently defined as hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or  
5 substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, or cycloalkyl and substituted cycloalkyl groups containing 5 to 12 carbon atoms, and their employment as initiators in the anionic polymerization of olefin containing monomers in  
10 an inert, hydrocarbon solvent optionally containing a Lewis base. The process reacts selected omega-thioprotected-1-haloalkyls whose alkyl groups contain 3 to 25 carbon atoms, with alkali metal, preferably lithium, at a temperature between about 35°C and about  
15 130°C, preferably at the reflux temperature of an alkane, cycloalkane or aromatic reaction solvent containing 5 to 10 carbon atoms and mixtures of such solvents.

Anionic polymerizations employing the  
20 monofunctional thioether initiators are conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal modifier, using an olefinic monomer which is an alkenylsubstituted aromatic hydrocarbon or a 1,3-diene at a temperature of  
25 about -30°C to about 150°C. The polymerization reaction proceeds from initiation to propagation and is finally terminated with appropriate reagents so that the polymer is mono-functionally or di-functionally terminated. The polymers may have a molecular weight  
30 range of about 1000 to 50,000 but the molecular weight can be higher. Typically 5 to 50 milli-moles of initiator is used per mole of monomer.

The initiator precursor, omega-thio-protected-1-haloalkanes (halides), can be prepared from  
35 the corresponding halothiol by standard literature methods. For example, 3-(1,1-dimethylethylthio)-1-propylchloride can be synthesized by the reaction of 3-

-21-

chloro-1-propanthiol with 2-methylpropene according to the method of A. Alexakis, M. Gardette, and S. Colin, Tetrahedron Letters, 29, 1988, 2951. Alternatively, reaction of 1,1-dimethylethylthiol with 1-bromo-3-chloropropane and a base affords 3-(1,1-dimethylethylthio)-1-propylchloride. The method of B. Figadere, X. Franck and A. Cave, Tetrahedron Letters, 34, 1993, 5893, which involves the reaction of the appropriate thiol with 2-methyl-2-butene catalyzed by boron trifluoride etherate, can be employed for the preparation of the t-amyl ethers. Additionally, 5-(cyclohexylthio)-1-pentylhalide and the like, can be prepared by the method of J. Almena, F. Foubelo, and M. Yus, Tetrahedron, 51, 1995, 11883. This synthesis involves the reaction of the appropriate thiol with an alkylolithium, then reaction of the lithium salt with the corresponding alpha, omega dihalide. 3-(Methylthio)-1-propylchloride can be prepared by chlorination of the corresponding alcohol with thionyl chloride, as taught by D. F. Taber and Y. Wang, J. Org. Chem., 58, 1993, 6470. Methoxymethylthio compounds, such as 6-(methoxymethylthio)-1-hexylchloride, can be prepared by the reaction of the omega-chloro-thiol with bromochloromethane, methanol, and potassium hydroxide, by the method of F. D. Toste and I. W. J. Still, Synlett, 1995, 159. T-Butyldimethylsilyl protected compounds, for example 4-(t-butyldimethylsilylthio)-1-butylhalide, can be prepared from t-butyldimethylchlorosilane, and the corresponding thiol, according to the method described in U.S. Patent No. 5,493,044.

Omega-thio-protected 1-haloalkanes prepared in accordance with this earlier process useful in practicing this invention include, but are not limited to, 3-(methylthio)-1-propylhalide, 3-(methylthio)-2-methyl-1-propylhalide, 3-(methylthio)-2,2-dimethyl-1-propylhalide, 4-(methylthio)-1-butylhalide, 5-

- 22 -

- (methylthio)-1-pentylhalide, 6-(methylthio)-1-hexylhalide, 8-(methylthio)-1-octylhalide, 3-(methoxymethylthio)-1-propylhalide, 3-(methoxymethylthio)-2-methyl-1-propylhalide, 3-
- 5 (methoxymethylthio)-2,2-dimethyl-1-propylhalide, 4-(methoxymethylthio)-1-butylhalide, 5-(methoxymethylthio)-1-pentylhalide, 6-(methoxymethylthio)-1-hexylhalide, 8-(methoxymethylthio)-1-octylhalide, 3-(1,1-
- 10 dimethylethylthio)-1-propylhalide, 3-(1,1-dimethylethylthio)-2-methyl-1-propylhalide, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propylhalide, 4-(1,1-dimethylethylthio)-1-butylhalide, 5-(1,1-dimethylethylthio)-1-pentylhalide, 6-(1,1-
- 15 dimethylethylthio)-1-hexylhalide, 8-(1,1-dimethylethylthio)-1-octylhalide, 3-(1,1-dimethylpropylthio)-1-propylhalide, 3-(1,1-dimethylpropylthio)-2-methyl-1-propylhalide, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propylhalide, 4-
- 20 (1,1-dimethylpropylthio)-1-butylhalide, 5-(1,1-dimethylpropylthio)-1-pentylhalide, 6-(1,1-dimethylpropylthio)-1-hexylhalide, 8-(1,1-dimethylpropylthio)-1-octylhalide, 3-(cyclopentylthio)-1-propylhalide, 3-(cyclopentylthio)-2-methyl-1-
- 25 propylhalide, 3-(cyclopentylthio)-2,2-dimethyl-1-propylhalide, 4-(cyclopentylthio)-1-butylhalide, 5-(cyclopentylthio)-1-pentylhalide, 6-(cyclopentylthio)-1-hexylhalide, 8-(cyclopentylthio)-1-octylhalide, 3-(cyclohexylthio)-1-propylhalide, 3-(cyclohexylthio)-2-
- 30 methyl-1-propylhalide, 3-(cyclohexylthio)-2,2-dimethyl-1-propylhalide, 4-(cyclohexylthio)-1-butylhalide, 5-(cyclohexylthio)-1-pentylhalide, 6-(cyclohexylthio)-1-hexylhalide, 8-(cyclohexylthio)-1-octylhalide, 3-(t-
- 35 butyldimethylsilylthio)-1-propylhalide, 3-(t-butyldimethylsilylthio)-2-methyl-1-propylhalide, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propylhalide, 3-(t-butyldimethylsilylthio)-2-methyl-1-propylhalide, 4-



-23-

(t-butyldimethylsilylthio)-1-butylhalide, 6-(t-butyldimethylsilylthio)-1-hexylhalide and 3-(trimethylsilylthio)-2,2-dimethyl-1-propylhalide. The halo- or halide group is preferably selected from chlorine and bromine.

Examples of functionalized organolithium initiators (II) include, but are not limited to, tert-alkoxy-alkyllithiums such as 3-(1,1-dimethylethoxy)-1-propyllithium and its more hydrocarbon-soluble isoprene chain-extended oligomeric analog (n=2), 3-(tert-butyldimethylsilyloxy)-1-propyllithium (n=0), tert-alkylthio-alkyllithiums such as 3-(1,1-dimethylethylthio)-1-propyllithium and its more hydrocarbon-soluble isoprene chain-extended oligomeric analog (n=2), 3-(dimethylamino)-1-propyllithium and its more hydrocarbon-soluble isoprene chain-extended oligomeric analog (n=2) and 3-(di-tert-butyldimethylsilylamino)-1-propyllithium, and mixtures thereof. Further examples of protected functionalized initiators that may be employed in this invention include, but are not limited to, 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-

- (t-butyltrimethylsilyloxy)-1-butyllithium, 5-(t-butyltrimethylsilyloxy)-1-pentyllithium, 6-(t-butyltrimethylsilyloxy)-1-hexyllithium, 8-(t-butyltrimethylsilyloxy)-1-octyllithium and 3-
- 5 (trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-
- 10 hexyllithium, 8-(dimethylamino)-1-propyllithium, 4-(ethoxy)-1-butyllithium, 4-(propyloxy)-1-butyllithium, 4-(1-methylethoxy)-1-butyllithium, 3-(triphenylmethoxy)-2,2-dimethyl-1-propyllithium, 4-(triphenylmethoxy)-1-butyllithium, 3-[3-
- 15 (dimethylamino)-1-propyloxy]-1-propyllithium, 3-[2-(dimethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diisopropylamino)-1-ethoxy]-1-propyllithium, 3-[2-(1-piperidino)-1-ethoxy]-1-propyllithium, 3-[2-(1-
- 20 pyrrolidino)-1-ethoxy]-1-propyllithium, 4-[3-(dimethylamino)-1-propyloxy]-1-butyllithium, 6-[2-(1-piperidino)-1-ethoxy]-1-hexyllithium, 3-[2-(methoxy)-1-ethoxy]-1-propyllithium, 3-[2-(ethoxy)-1-ethoxy]-1-propyllithium, 4-[2-(methoxy)-1-ethoxy]-1-butyllithium,
- 25 5-[2-(ethoxy)-1-ethoxy]-1-pentyllithium, 3-[3-(methylthio)-1-propyloxy]-1-propyllithium, 3-[4-(methylthio)-1-butyloxy]-1-propyllithium, 3-(methylthiomethoxy)-1-propyllithium, 6-[3-(methylthio)-1-propyloxy]-1-hexyllithium, 3-[4-(methoxy)-benzyloxy]-
- 30 1-propyllithium, 3-[4-(1,1-dimethylethoxy)-benzyloxy]-1-propyllithium, 3-[2,4-(dimethoxy)-benzyloxy]-1-propyllithium, 8-[4-(methoxy)-benzyloxy]-1-octyllithium, 4-[4-(methylthio)-benzyloxy]-1-butyllithium, 3-[4-(dimethylamino)-benzyloxy]-1-
- 35 propyllithium, 6-[4-(dimethylamino)-benzyloxy]-1-hexyllithium, 5-(triphenylmethoxy)-1-pentyllithium, 6-(triphenylmethoxy)-1-hexyllithium, and 8-

-25-

- (triphenylmethoxy)-1-octyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-butyl dimethylsilylthio)-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2,2-dimethyl-1-propyllithium, 10 4-(t-butyl dimethylsilylthio)-1-butyllithium, 6-(t-butyl dimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium and their more hydrocarbon soluble conjugated alkadiene, alkenylsubstituted aromatic hydrocarbon, and mixtures thereof, chain extended oligomeric analogs (n = 1-5).
- 30 Functionalized copolymers of Formula (I) can be further reacted with other comonomers such as di- or polyesters, di- or polyisocyanates, di-, poly-, or cyclic amides, di- and polycarboxylic acids, and di- and polyols in the presence of a strong acid catalyst to simultaneously deprotect the functional copolymer and polymerize both functional ends thereof to produce novel segmented block polymers. Alternatively,
- 35

-26-

functionalized copolymers of Formula (I) can be reacted with other comonomers in the absence of a strong acid catalyst to yield block copolymers, while maintaining the integrity of the protective group to provide a  
5 functional block copolymer. Still another alternative is to remove the protective group of the functional copolymer of Formula (I) and to polymerize a functional block copolymer of the preceding sentence with the same or other comonomers to produce novel segmented block  
10 polymers.

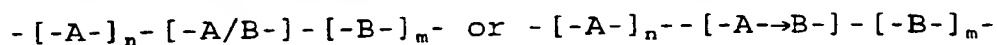
The polymerization solvent can be an inert solvent such as a hydrocarbon. Solvents useful in practicing this invention include, but are not limited to, inert liquid alkanes, cycloalkanes and aromatic  
15 solvents such as alkanes and cycloalkanes containing five to ten carbon atoms, such as pentane, hexane, cyclohexane, methylcyclohexane, heptane, methylcycloheptane, octane, decane and the like, and aromatic solvents containing six to ten carbon atoms  
20 such as toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, n-propylbenzene, isopropylbenzene, n-butylbenzene, and the like.

Polar solvents can also be used, including, but not limited to, diethyl ether, dibutyl ether,  
25 tetrahydrofuran, 2-methyltetrahydrofuran, methyl tert-butyl ether, diazabicyclo[2.2.2]octane, triethylamine, tributylamine, N,N,N',N'-tetramethylethylene diamine (TMEDA), and 1,2-dimethoxyethane (glyme). Polar solvents (modifiers) can also be added to the  
30 polymerization reaction to alter the microstructure of the resulting polymer or to promote functionalization or randomization. The amount of the polar modifier added depends on the vinyl content desired, the nature of the monomer, the temperature of the polymerization,  
35 and the identity of the polar modifier.

The skilled artisan will appreciate that copolymerization of a mixture of alkenylsubstituted

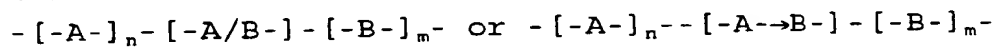
-27-

aromatic monomers and conjugated diene monomers in a hydrocarbon solvent results in the preferential incorporation of the conjugated diene compound to form tapered (or graded) block copolymers with compositional  
 5 heterogeneity incorporated intramolecularly along the polymer chain. The monomer sequence distribution can be described schematically by (1) below:



wherein A is a saturated or unsaturated hydrocarbyl  
 10 group derived by incorporation of a conjugated diene; n represents the equivalents of A employed primarily in the initial block segment; B is an aromatic substituted saturated hydrocarbyl group derived by incorporation of an alkenylsubstituted aromatic hydrocarbon; and m  
 15 represents the equivalents of B employed primarily in the second block segment.

This sequence is reversed when a mixture of alkenylsubstituted aromatic hydrocarbons and conjugated dienes is polymerized in a polar solvent. Accordingly,  
 20 the alkenylsubstituted aromatic hydrocarbon is preferentially incorporated to form a tapered (or graded) block copolymer, schematically illustrated by (2) below:



25 wherein A is an aromatic substituted saturated hydrocarbyl group derived by incorporation of an alkenylsubstituted aromatic substituted hydrocarbon; n represents the equivalents of A employed primarily in the initial block segment; B is a saturated or  
 30 unsaturated hydrocarbyl group derived by incorporation of a conjugated diene; and m represents the equivalents of B employed primarily in the second block segment.

A telechelic di-protected functional copolymer having random, tapered or sequential blocks  
 35 can be formed by reacting the living copolymer with a difunctional linking agent, such as ethylbenzoate, xylene dibromide or dimethyldichlorosilane. In the

-28-

case of the sequential or tapered block copolymer, this linking reaction results in a telechelic triblock copolymer with protected functionality. These triblock polymers may optionally be hydrogenated before or after  
5 removal of the protecting groups to produce saturated difunctional polymers. In the case of protected hydroxy functional polymers, the deprotection will yield a telechelic dihydroxyl functional polymer which may then be further reacted with bisphenol A and  
10 phosgene, caprolactam and adipic acid, hexamethylene diamine and adipic acid, dimethyl terephthalate and 1,4-butane diol, or diphenylmethane diisocyanate, which would produce, respectively, sequential pentablock polymers with blocks of polyamide, polyester and  
15 polyurethane attached to the selectively deprotected telechelic functional polydiene/polyarylethylene or polyolefin/polyarylethylene triblocks.

As noted above, if desired, the protecting groups can be removed from the copolymer. Deprotection  
20 can be performed either prior to or after the optional hydrogenation of the residual aliphatic unsaturation. For example, to remove tert-alkyl-protected groups, the protected polymer can be mixed with Amberlyst® 15 ion exchange resin and heated at an elevated temperature,  
25 for example 150°C, until deprotection is complete. Tert-alkyl-protected groups can also be removed by reaction of the polymer with para-toluensulfonic acid, trifluoroacetic acid, or trimethylsilyliodide. Additional methods of deprotection of the tert-alkyl  
30 protecting groups can be found in T.W. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, Second Edition, Wiley, New York, 1991, page 41.

Tert-butyldimethylsilyl protecting groups can be removed by treatment of the copolymer with acid,  
35 such as hydrochloric acid, acetic acid, para-toluensulfonic acid, or Dowex® 50W-X8. Alternatively, a source of fluoride ions, for instance tetra-n-

-29-

butylammonium fluoride, potassium fluoride and 18-crown-6, or pyridine-hydrofluoric acid complex, can be employed for deprotection of the tert-butyltrimethylsilyl protecting groups. Additional methods of deprotection of the tert-butyltrimethylsilyl protecting groups can be found in T.W. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, Second Edition, Wiley, New York, 1991, pages 80-83.

In addition, protecting groups can be selectively removed from the polymer, i.e., deprotecting conditions can be selected so as to remove at least one protecting group without removing other dissimilar protecting groups, by proper selection of deprotecting reagents and conditions.

The following table details representative experimental conditions capable of selectively removing protecting groups (more labile) while maintaining the integrity of other different protecting groups (more stable).

	<u>Labile</u>	<u>Stable</u>	<u>Conditions</u>
20	t-butyltrimethylsilyl	t-butyl	tetrabutylammonium fluoride
	t-butyltrimethylsilyl	t-butyl	1 N HCL
	t-butyltrimethylsilyl	dialkylamino	tetrabutylammonium fluoride
	t-butyltrimethylsilyl	dialkylamino	1 N HCL
25	t-butyl	dialkylamino	Amberlyst® resin
	t-amyl	dialkylamino	Amberlyst® resin
	trimethylsilyl	t-butyl	tetrabutylammonium fluoride
	trimethylsilyl	t-butyl	1 N HCL
	trimethylsilyl	dialkylamino	tetrabutylammonium fluoride
30	trimethylsilyl	dialkylamino	1 N HCL

The progress of the deprotection reactions can be monitored by conventional analytical techniques, such as Thin Layer Chromatography (TLC), Nuclear Magnetic Resonance (NMR) spectroscopy, or InfraRed (IR) spectroscopy.

-30-

Examples of methods to hydrogenate the copolymers of this invention are described in U.S. Patent Nos. 4,970,254, 5,166,277, 5,393,843 and 5,496,898, the entire disclosure of each of which is incorporated by reference. The hydrogenation of the copolymer is conducted *in situ*, or in a suitable solvent, such as hexane, cyclohexane or heptane. This solution is contacted with hydrogen gas in the presence of a catalyst, such as a nickel catalyst. The hydrogenation is typically performed at temperatures from 25°C to 150°C, with a archetypal hydrogen pressure of 15 psig to 1000 psig. The progress of this hydrogenation can be monitored by InfraRed (IR) spectroscopy or Nuclear Magnetic Resonance (NMR) spectroscopy. The hydrogenation reaction is conducted until at least 90% of the aliphatic unsaturation has been saturated. The hydrogenated copolymer is then recovered by conventional procedures, such as removal of the catalyst with aqueous acid wash, followed by solvent removal or precipitation of the copolymer.

In another aspect of the invention, multi-branched or star-shaped polymers which include alkenylsubstituted aromatic- and conjugated diene-based compounds are also provided, including multi-branched or star-shaped polymers with protected functional groups, their optionally hydrogenated analogues, and the polymers produced by removal of the protecting groups. The star polymers in this aspect of the invention can be produced using the functional initiators (II) described above (singly or combinations thereof), which, by design, incorporate the versatility of functional branch end star polymers. For example, hydroxy-, thio-, or amino-terminated functional branches can be copolymerized with comonomers, such as organic diacids (such as carboxylic acids), diisocyanates, and the like. The copolymers can also include non-functional branches in the polymer. This



-31-

can provide improved impact resistance in molecules resulting from further copolymerization of the star-shaped polymers of the invention with other functional comonomers, for example, resultant polyester and/or polyamide molecules.

Novel multi-branched or star-shaped polymers having functional ends can be produced by polymerizing the alkenylsubstituted aromatic hydrocarbons and conjugated dienes as a mixture or sequentially as described above with protected functional organolithium initiators of Formula (II) (singly or as combinations thereof to provide arms having different protecting groups and/or different functional groups), and subsequently reacting the resulting copolymer with multifunctional linking agents. This can lead to polymer anion chain lengths of approximately the same size.

Examples of useful linking or coupling agents include halosilanes, such as silicon tetrachloride and methyl trichlorosilane; halostannanes, such as tin tetrachloride; phosphorus halides, such as phosphorus trichloride; and isomeric (mixtures of *ortho*, *meta* and *para*) dialkenylaryls and isomeric di- and trivinylaryls, such as 1,2-divinylbenzene, 1,3-divinylbenzene, 1,4-divinylbenzene, 1,2,4-trivinylbenzenes, 1,3-divinylnaphthalenes, 1,8-divinylnaphthalene, 1,2-diisopropenylbenzene, 1,3-diisopropenylbenzene, 1,4-diisopropenylbenzene, 1,3,5-trivinylbenzene, and other suitable materials known in the art to be useful for coupling polymers, as well as mixtures of coupling agents. See also U.S. Patent Nos. 3,639,517 and 5,489,649, and R.P. Zelinski et al in J.Polymer.Sci., A3, 93, (1965) for these and additional coupling agents. Mixtures of coupling agents can also be used. Generally, the amount of coupling agent used is such that the molar ratio of protected living polymer anions to coupling agents

-32-

ranges from 1:1 to 24:1. This linking process is described, for example, in U.S. Patent No. 4,409,357 and by L.J. Fetters in *Macromolecules*, 9,732 (1976).

These radiating multi-arm polymers with  
5 protected functionality on the ends of the arms may be optionally hydrogenated before or after removal of the protecting groups. The star polymers thus formed may have hydroxyl, thio, and/or amino functional branch ends.

10 Nonfunctional initiators (such as n-butyllithium, sec-butyllithium, and tert-butyllithium) may also be mixed with the functional initiators of Formula (II) to provide non-functional branch ends as well, which can serve to modify the physical properties  
15 of these star-shaped or radiating polymers, especially after their further copolymerization with other functional monomers, such as organic diacids or organic diisocyanates.

Alternatively, novel multi-branched or star-  
20 shaped polymers possessing functional ends which may be the same or different, and/or both functional and non-functional ends, may be produced by separately polymerizing alkenylsubstituted aromatic hydrocarbons and conjugated dienes with protected functional  
25 initiators (II) and/or with non-functional organolithium initiators, subsequently mixing the resulting separately produced anions, treating the resulting mixture with multifunctional linking agents, and optionally hydrogenating before or after optionally  
30 deprotecting the functional ends of the polymer. This alternative method allows for control of the molecular weight of the arms of the star polymer (for example, different polymer anion chain lengths can be produced) and provides for a more selective control of the  
35 physical properties of the resultant polymers.

If desired, the protecting groups can be removed from the arms of the star polymer, prior to or

-33-

after the optional hydrogenation of the residual unsaturation of the arms, using the techniques described above. This includes selective deprotection when dissimilarly protected functional groups are present, as detailed above.

Molecular weights of the resulting linked or coupled polymers can vary depending on the molecular weight of the polymer anion and the number of potential functional linking groups on a coupling agent. The sizes of the branches of the linked polymer can be the same or vary.

A wide variety of symmetrically and asymmetrically functional polymers may be produced by reacting the living copolymer resulting from the copolymerization of alkenylsubstituted aromatic and conjugated dienes described above with various functionalizing agents. For example, addition of carbon dioxide (see *J. Polym. Sci., Polym. Chem.* 30, 2349 (1992)) to a living copolymer produced using the protected functional initiator 3-(tert-butoxy)-1-propyllithium, chain-extended with two equivalents of isoprene, would produce a polymer with one protected hydroxyl and one carboxyl group. The living copolymer may also be reacted with 1,5 diazabicyclo-(3.1.0) hexane as described in U.S. Patent No. 4,753,991 to produce a polymer with one protected hydroxyl and one amino group. A polymer with one protected hydroxyl group and one protected amino group can be prepared by reaction of the living copolymer with a protected amino propyl bromide, see *Macromolecules*, 23, 939 (1990), or with N-(benzylidene)trimethylsilylamine (see *British Polymer Journal*, 22, 249 (1990)). Reaction of the living copolymer with oxetane or substituted oxetanes (see U.S. Patent No. 5,391,637) would afford a copolymer which contained one protected hydroxyl and a hydroxyl group. A polymer with two protected hydroxyl groups can be prepared by reaction of the living

-34-

copolymer with a silicon derived acetal, see U.S. Patent No. 5,478,899.

Other asymmetrically substituted polymers may be produced having epoxy or isocyanate groups at one end, for example, by reacting the lithium salt of a protected hydroxy-terminated living copolymer (before hydrolysis), with epichlorohydrin or, by reacting the living copolymer itself with an equivalent of a diisocyanate, such as methylene 4,4-diphenyl diisocyanate (2/1 NCO/OH). These unsymmetrically substituted polymers could then be further reacted with other comonomers either with or without simultaneous deprotection as described below.

The polar functional groups of the polymer chain ends allow the polymers of this invention to alter the surface properties of polymers like polyethylene (including high density polyethylene, low density polyethylene and linear low density polyethylene), polypropylene, polyisobutylene and copolymers and blends thereof. When the polymers of this invention are blended with non-polar polyolefins, the polar functional groups on the chain ends, being incompatible with the non-polar polyolefin, will phase separate and migrate to the surface of the polyolefin. The functional polymers of the invention can be added in amounts ranging from 1 to 25% by weight based on the weight of the polyolefin. Properties such as surface adhesion are thus greatly enhanced, leading to improved adhesion of pigments in printing inks for labels, composite layering, and other adhesive applications. An alternative approach to modification of polymer surfaces to alter properties by introduction of functional groups has been the use of chemical reagents such as alkylolithiums (see, for example, A.J. Dias, K-W Lee, and T.J. McCarthy, Rubber & Plastics News, 18-20, October 31, 1988, and A.J. Dias and T.J. McCarthy, Macromolecules, 20, 1437 (1987)).

-35-

Protected monohydroxy copolymers alone and in their hydrogenated forms can be used as base materials to lend flexibility and higher impact strength in a number of formulas to produce coatings, sealants, binders and block copolymers with polyesters, polyamides and polycarbonates as described in UK Patent Application GB2270317A and in "Polytail" data sheets and brochures (Mitsubishi Kasei America).

In the presence of acidic catalysts used to promote the formation of many of these block copolymer resins, the protective group of the hydrogenated polymer is removed as well, allowing the exposed hydroxyl grouping in the base polymer molecule to simultaneously participate in the block copolymer reaction.

For example, hydrogenated hydroxy-terminated copolymers may be reacted with bisphenol A and phosgene in the presence of appropriate catalysts with simultaneous deprotection to yield a polycarbonate alternating block copolymer. The resulting products are useful as molding resins, for example, to prepare interior components for automobiles.

A segmented polyamide-hydrogenated block copolymer is also useful as a molding composition to prepare exterior automotive components and can be prepared by reacting a hydrogenated hydroxy-terminated copolymer with, for example, caprolactam and adipic acid in the presence of a suitable catalyst.

A segmented polyester-hydrogenated block copolymer is produced by reaction of hydrogenated hydroxy-terminated copolymer with dimethyl terephthalate and a suitable acidic catalyst. Again, the products are useful as molding compounds for exterior automotive components.

Isocyanate-terminated prepolymers can be produced from hydrogenated hydroxy-terminated copolymers by reaction with suitable diisocyanates (2/1

-36-

- NCO/OH) as above and which can be further reacted with diols and additional diisocyanates to form segmented polyurethanes useful for water based, low VOC coatings. Inclusion of acid functional diols, such as
- 5 dimethylolpropionic acid, in the polyurethane introduces pendant carboxyl groups which can be neutralized with tertiary amines to afford water dispersable polyolefin/polyurethane segmented polymers, useful for water based coatings. This same principle
- 10 could be applied to acrylic polymers made with tertiary amine functional monomers included, which could be made by free radical polymerization following reacting the hydroxyl groups at the terminal ends of the polymer with acryloyl chloride or methacryloyl chloride.
- 15 Segmented polyurethane prepolymers may be mixed with tackifying resins and used as a moisture-curable sealant, caulk or coating.

Another possible application in coatings would be the use of new dendrimers, based on the use of

20 the polymer with hydroxyl functionality at the termini thereof to form the core for dendritic hybrid macromolecules based on condensation or addition polymerizations, utilizing the hydroxyl functionality as the initiating site (see, for example Gitsov and

25 Frechet, American Chemical Society PMSE Preprints, Volume 73, August 1995.

Yet another application includes use as toughening polymers for epoxy composites, utilizing the polymer core with the hydroxyl groups converted to half

30 esters by reaction with anhydrides. These epoxy reactive polymers can then be utilized as reactants with epoxy resins and amines in composite systems. Reacting the hydroxyl functional polymers into unsaturated polyesters provides a new polymer

35 toughening system for polyester molding compounds for automotive and other uses. For a review of the use of linear polymers for toughening of epoxies and

-37-

polyesters, see "Rubber-Toughened Plastics", Edited By C.Keith Riew, ACS Advances in Chemistry Series ,#222.

Cathodic electrodepositable coatings may be prepared from epoxy functional polymers described above  
5 by reacting with epoxy resins in the presence of excess amine or polyamine, to completely react all the epoxy groups, distilling off excess amine, and neutralizing the resulting epoxy-amine adduct with water soluble organic or inorganic acids to form water soluble,  
10 quarternary ammonium containing polymer salts (see for reference, U.S. Patent Nos. 3,617,458, 3,619,398, 3,682,814, 3,891,527, 3,947,348, and 4,093,594). Alternatively, the above epoxy-amine polymer adducts may be converted to quarternary phosphonium or  
15 sulfonium ion containing polymers, as described in U.S. Patent No. 3,935,087.

An acrylate-terminated prepolymer curable by free-radical processes can be prepared from the hydrogenated hydroxy-terminated copolymer by reaction  
20 with a diisocyanate (2NCO/OH) followed by further reaction with hydroxyethyl acrylate in the presence of a basic reagent.

Another likely application for acrylate or methacrylate terminated hydrogenated polymers includes  
25 use as viscosity index (V.I.) improvers. Using carboxyl functional monomers, such as acrylic acid and methacrylic acid, and/or amine functional monomers such as acrylamide, along with free radical initiators in further polymerizations, can result in the formation of  
30 polymer segments at the periphery of each termini with amine or other functionalities which, in addition to the advantageous properties of the polymers as V.I. improvers, combines the ability to add functionality to the polymers for dispersant properties (see, for  
35 example, U.S. Patent Nos. 5,496,898, 4,575,530, 4,486,573, 5,290,874, and 5,290,868).

-38-

The versatility of the hydroxyl functional polymers of this invention, and the wide range of different segmented polymers (polyethers, polyesters, polyamides, polycarbonates, polyurethanes, etc.) which  
5 can be initiated at the hydroxyl groups, leads to numerous possible applications as compatibilizers for polymer blends and alloys. In addition to the use of such blends for new applications, much recent interest is generated in the use of compatibilizers to  
10 facilitate polymer waste recycling.

Alternatively, protecting groups may be removed, either before or after optional hydrogenation of the aliphatic unsaturation, then the hydroxy terminated polymer may be reacted with functional  
15 comonomers to produce novel copolymers using these and other processes. Thus, for example, a hydroxy terminated polymer may be hydrogenated, and then reacted with ethylene oxide in the presence of potassium tert-butoxide to produce a poly(ethylene  
20 oxide)-hydrogenated block copolymer. This reaction sequence affords a hydrogel.

Alternatively, the protected monohydroxy terminated copolymer may be reacted with functional comonomers, without simultaneously removing the  
25 protective group. These copolymers then may be deprotected and then further reacted with the same or different comonomers to form yet other novel copolymers. Thus, for example, a hydroxyterminated copolymer may be hydrogenated, and then reacted with  
30 ethylene oxide in the presence of potassium tert-butoxide to produce a poly(ethylene oxide)-hydrogenated polystyrene/polydiene copolymer with one protected hydroxyl group on the polystyrene segment. This hydroxyl can then be deprotected and a poly(ethylene  
35 oxide) polymer having different chain lengths grown onto both ends of the polystyrene/polydiene segment.



-39-

In another possible application, the living copolymer may be reacted with an alkenylarylhalosilane such as styrenyldimethylchlorosilane to yield the corresponding omega-styrenyl terminated macromonomer according to the teachings of U.S. Patent No. 5,278,244, which may then be further polymerized by a variety of techniques to yield "comb" polymers which, on deprotection and hydrogenation yield branched polymers with hydroxyfunctionality on the branch-ends. Such multi-functionality can be utilized to graft a water-soluble polymer such as polyethylene oxide onto a hydrophobic polyolefinic core to produce hydrogels.

In still another possible application, hydrogenated hydroxyterminated branches of the polymers may be further reacted with acryloyl chloride or methacryloyl chloride, and the resultant acrylate or methacrylate-terminated polymer further polymerized with monomers selected from the group of alkyl acrylates, alkyl methacrylates, and dialkylacrylamides to produce hydrogels. Further, acrylate or methacrylate-terminated polymers may be polymerized by free-radical processes.

The following examples further illustrate the invention.

#### 25 General Procedure

All reagents (monomers, solvent, and additives) were purified as described by Morton and Fetters in "Anionic Polymerization of Vinyl Monomers," *Rubb. Chem. Tech.*, 48, 3, 1975. High vacuum techniques for the polymerization reactions were also performed as specified by the aforementioned article.

-40-

## PREPARATION OF THE INITIATORS

## Example A

Preparation of 3-(t-Butyldimethylsilyloxy)-1-Propyllithium Chain Extended with 2 Moles of Isoprene

5 A 500 ml, three-necked Morton flask was equipped with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermocouple, a reflux condenser, and an argon inlet. This apparatus was dried in an oven  
10 overnight at 125°C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium dispersion was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml), then dried in a stream of argon. The dry dispersion, 5.20 grams (0.749  
15 mole, 2.80 equivalents) was transferred to the flask with 260 ml cyclohexane. This suspension was stirred at 450 RPMs, and heated to 65°C with a heating mantle. The heat source was removed. 1-(t-Butyldimethylsilyloxy)-3-chloro-propane, 58.82 grams  
20 (0.268 mole, 1.00 equivalent) was added dropwise. An exotherm was detected after 31.8% of the feed had been added. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 60-65°C. The total feed time was one hundred five minutes. An  
25 exotherm was noted until the last drop of feed was added, then the temperature fell off rapidly to room temperature. The reaction mixture was stirred at room temperature for forty five minutes, then heated to 65°C with a heating mantle. The heat source was removed.  
30 Isoprene, 36.45 grams (0.535 mole, 2.00 equivalents) was then added dropwise. An exotherm was noted after 24.6% of the feed had been added. Hexane cooling was applied to maintain the reaction temperature at 60-65°C. The total isoprene feed time was thirty eight  
35 minutes. The reaction mixture was allowed to stir at room temperature for one hour, then transferred to a small pressure filter with argon pressure. Very rapid filtration was observed with 2 psi argon. The muds

-41-

were reslurried with cyclohexane (2 X 50 ml). This afforded an orange solution, yield = 530 ml, 425.34 grams. Total base = 17.1 wt. %; Active C-Li = 15.9 wt %; Yield (based on active C-Li) = 80.8%.

### Example B

Preparation of 3-(t-Butyldimethylsilylthio)-1-propyllithium Chain Extended with 2 Moles of Isoprene

A 500 ml, three-necked Morton flask is equipped with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermocouple, a reflux condenser, and an argon inlet. This apparatus is dried in an oven overnight at 125°C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium dispersion is washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml), then dried in a stream of argon. The dry dispersion, 5.20 grams (0.749 mole, 2.80 equivalents) is transferred to the flask with 260 ml cyclohexane. This suspension is stirred at 450 RPMs, and heated to 65°C with a heating mantle. The heat source is removed. 1-(t-Butyldimethylsilylthio)-3-chloro-propane, 60.22 grams (0.268 mole, 1.00 equivalent) is added dropwise. An exotherm is detected after 21.8% of the feed has been added. A dry ice/hexane cooling bath is applied to maintain the reaction temperature at 60-65°C. The total feed time is one hundred minutes. An exotherm is noted until the last drop of feed is added, then the temperature falls off rapidly to room temperature. The reaction mixture is stirred at room temperature for forty five minutes, then heated to 65°C with a heating mantle. The heat source is removed. Isoprene, 36.45 grams (0.535 mole, 2.00 equivalents) is then added dropwise. An exotherm is noted after 24.6% of the feed has been added. Hexane cooling is applied to maintain the reaction temperature at 60-65°C. The total isoprene feed time is thirty eight minutes. The

-42-

reaction mixture is allowed to stir at room temperature for one hour, then transferred to a small pressure filter with argon pressure. Very rapid filtration is achieved with 2 psi argon. The muds are reslurried with cyclohexane (2 X 50 ml). This affords an orange solution; yield = 530 ml, 435.21 grams. Total base = 17.7 wt. %; Active C-Li = 16.9 wt %; Yield (based on active C-Li) = 82.4%.

## Example C

10     *Preparation of 3-(N,N-Dimethylamino)-1-propyllithium*  
         *Chain Extended with 2 Moles of Isoprene*

A 500 ml, three-necked Morton flask was equipped with a mechanical stirrer, a 125 ml pressure-equalizing addition funnel, and a Claisen adapter fitted with a thermocouple, a reflux condenser, and an argon inlet. This apparatus was dried in an oven overnight at 125°C, assembled hot, and allowed to cool to room temperature in a stream of argon. Lithium dispersion was washed free of mineral oil with hexane (2 X 70 ml), and pentane (1 X 70 ml), then dried in a stream of argon. The dry dispersion, 10.57 grams (1.520 moles) was transferred to the flask with 250 ml cyclohexane. Coarse sand, 45.3 grams, was added to the reaction mixture. This suspension was stirred at 600-675 RPMs, and heated to 37°C with a heating mantle. The heat source was removed. 1-Chloro-3-(N,N-dimethylamino)propane, 19.64 grams (0.1615 mole) dissolved in 120 ml. Cyclohexane was added dropwise. An exotherm (up to 52°C) was detected after 7% of the feed had been added. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 41-44°C. The total feed time was thirty-two minutes. An exotherm was noted until the last drop of feed was added, then the temperature was maintained at 36-40°C for an additional thirty minutes. The reaction mixture was then transferred to a sintered glass filter while

-43-

still warm. The filtration was complete in three minutes with three psi argon pressure. This afforded a hazy suspension. Yield = 400 ml, 298.2 grams. Active C - Li = 0.361 M (0.469 m/kg) at 40°C. Yield (based on 5 active C - Li = 87%.

The product crystallized from solution upon standing at room temperature. The concentration of the clear supernatant solution was about 0.3 M.

A dry 500 ml round bottom flask was fitted 10 with a magnetic stir bar, and an argon inlet. This apparatus was purged with argon, then 154.77 grams (0.0726 mole) of the suspension prepared above was added to the flask. Isoprene, 9.4 grams (0.138 mole, 1.90 equivalents) was then added all at once. The 15 reaction mixture was then heated to 48-49°C for forty minutes. This afforded a slightly hazy golden solution, which was partially vacuum-stripped on the rotary evaporator to afford the product solution. Yield = 43.32 grams. Active C - Li = 1.36 M (1.65 20 m/kg). Recovered yield (based on active C - Li) = 98.5%.

## EXAMPLES OF THE INVENTION - PREPARATION OF POLYMERS

### EXAMPLE 1

25 Preparation of Poly(Styrene-Block-Isoprene) Diblock and Poly(Styrene-Block-Isoprene-Block-Isoprene) Triblock Copolymers

After thorough evacuation and filling with dry argon, an all-glass, high vacuum reactor was charged with 0.44 mmols of 3-t-butoxy-propyllithium 30 (0.83 mL, 0.53 M in toluene, chain extended with 2 units of isoprene) under a positive argon pressure. After evacuation, 250 mL of purified and dry benzene was distilled directly into the reactor, followed by removal from the vacuum line by heat sealing with a 35 hand torch. Then 3.06 g (29.4 mmol) of purified styrene was added by breaking the breakseal on the

-44-

respective ampoule. After stirring for 8 hours at 25°C, an aliquot was removed and terminated by degassed methanol. To the remainder of the sample, 5.99 g (87.9 mmol) of purified isoprene were added via an attached  
5 ampoule. After 16 hours of stirring at 25°C, the reaction was divided into three ampoules and one sample was terminated by addition of degassed methanol. The resulting terminated polymers were precipitated into methanol and dried in a vacuum oven. The polystyrene  
10 base polymer was analyzed by SEC and exhibited an  $M_n = 6,900$  g/mol and  $M_w/M_n = 1.08$ . The block copolymer was analyzed by SEC and by  $^1\text{H}$  NMR spectroscopy. The polymer molecular weight by SEC analysis (polyisoprene standards) corresponded to  $M_n = 20,500$  g/mol and  $M_w/M_n =$   
15 1.06. An  $^1\text{H}$  NMR resonance at  $\delta = 1.17$  ppm corresponding to the  $(\text{CH}_3)_3\text{CO-}$  unit was observed. The isoprene microstructure corresponded to 95% 1,4-units as determined by  $^1\text{H}$  NMR.

A sample of the living poly(styrene-block-isoprenyl)lithium was coupled with  
20 dichlorodimethylsilane (DDS) by slow addition of a 2% solution of DDS in benzene. SEC analysis of the resulting  $\alpha,\omega$ -difunctionalized triblock copolymer indicated that the coupling efficiency was 95%.

25

## EXAMPLE 2

Preparation of Poly(Styrene-Random-Isoprene) Copolymer

After thorough evacuation and filling with dry argon, an all-glass, high vacuum reactor was charged with 0.32 mmols of 3-t-butoxy-propyllithium  
30 (1.06 mL, 0.3 M in toluene, chain extended with 2 units of isoprene) under a positive argon pressure. After evacuation, 250 mL of purified and dry benzene was distilled directly into the reactor, followed by removal from the vacuum line by heat sealing with a  
35 hand torch. Then 3.16 g (30.3 mmol) of purified styrene and 6.50 g (95.4 mmol) of purified isoprene

-45-

were added via attached ampoules. An ampoule containing  $1.27 \times 10^{-5}$  mmol of potassium t-amylate ( $[\text{Li}]/[\text{K}] = 25$ ) in benzene was immediately added to promote randomization by breaking the respective  
5 breakseal. After 16 hours of stirring at  $25^\circ\text{C}$ , the reaction was terminated by addition of degassed methanol. The resulting polymer was precipitated into methanol and dried in a vacuum oven. The polymer was analyzed by SEC and by  $^1\text{H}$  NMR spectroscopy. The polymer  
10 molecular weight by SEC analysis (polyisoprene standards) corresponded to  $M_n = 35,200$  g/mol and  $M_w/M_n = 1.05$ . An  $^1\text{H}$  MNR resonance at  $\delta = 1.17$  ppm corresponding to the  $(\text{CH}_3)_3\text{CO}-$  unit was observed. The isoprene microstructure corresponded to 85% 1,4-units as  
15 determined by  $^1\text{H}$  NMR.

## EXAMPLE 3

Preparation of Poly(Styrene-Tapered-Isoprene) Copolymer

After thorough evacuation and filling with dry argon, an all-glass, high vacuum reactor was  
20 charged with 0.681 mmols of 3-t-butoxy-propyllithium (2.27 mL, 0.3 M in toluene, chain extended with 2 units of isoprene) under a positive argon pressure. After evacuation, 200 mL of purified and dry benzene was distilled directly into the reactor, followed by  
25 removal from the vacuum line by heat sealing with a hand torch. Then 1.02 g (9.79 mmol) of purified styrene and 16.00 g (234.8 mmol) of purified isoprene were added via attached ampoules. The reaction was frozen at  $-78^\circ\text{C}$  and then the side arms with ampoules  
30 were removed by heat sealing with a hand torch to minimize the reactor head space. After 8 hours of stirring at  $50^\circ\text{C}$ , the reaction was terminated by addition of degassed methanol. The resulting polymer was precipitated into methanol and dried in a vacuum  
35 oven. The polymer was analyzed by SEC and by  $^1\text{H}$  NMR spectroscopy. The polymer molecular weight by SEC

-46-

analysis (polyisoprene standards) corresponded to  $M_n = 25,200$  g/mol and  $M_w/M_n = 1.04$ . An  $^1\text{H}$  MNR resonance at  $\delta = 1.17$  ppm corresponding to the  $(\text{CH}_3)_3\text{CO-}$  unit was observed. The isoprene microstructure corresponded to 87% 1,4-units as determined by  $^1\text{H}$  NMR.

## EXAMPLE 4

Preparation of Poly(Styrene-Block-Isoprene) Copolymer

Two ampoules were prepared containing 2.73 g (26.2 mmol) of styrene and 8.18 g (120.1 mmol) isoprene, respectively, and attached to the reactor. Following, 0.525 mmol of initiator (0.53 M in toluene) was added to the reaction flask via syringe, the reactor sealed off, and the system evacuated. After vacuum distill ~250 ml of benzene as solvent into the reactor, the system was sealed off from the vacuum line. The styrene monomer was introduced into the flask by the way of a breakseal, where initiation occurred, as evidenced by the development of an orange color. The styrene was allowed to react for 8 hours at 25°C. Following, the isoprene monomer was added, and the reaction mixture assumed the characteristic pale yellow color. The isoprene block was allowed to propagate for 16 hours at 25°C. A small sample of the solution was terminated for analysis, while the remainder of the solution was divided among three 100 ml ampoules that were sealed off individually to be used further for coupling reactions.

## EXAMPLE 5

Preparation of Poly(Styrene-Random-Isoprene) Copolymer

Using a standard high vacuum reaction system, 1.00 g (9.60 mmol) of styrene and 1.50 g (22.0 mmol) of isoprene are added simultaneously to a solution of 0.191 mmol of initiator and 0.880 mmol THF in ~150 ml benzene. The reaction solution took on a pale orange color and was stirred at 25°C for 16 hours. The system



-47-

was terminated with methanol, precipitated, and analyzed.

## EXAMPLE 6

Preparation of Poly(Styrene-Taper-Isoprene) Copolymer

5 In a high vacuum system, 1.05 g (10.1 mmol) of styrene and 13.95 g (204.8 mmol) of isoprene are added simultaneously to a solution of 0.254 mmol 3-(N,N-dimethylamino)-1-propyllithium in ~200 ml benzene. After addition of the monomers, the reaction mixture is  
10 frozen, and the reactor arm holding the monomer ampoules is sealed off in order to produce a minimum of headspace within the reactor and maximize the incorporation of the volatile isoprene monomer to assure a styrene block at the termination of the  
15 reaction. The reaction proceeds at 50°C for 8 hours. The reaction is then terminated with purified methanol, precipitated, and analyzed.

## EXAMPLE 7

Preparation of Poly(Styrene-Random-Butadiene) Copolymer

20 A polystyrene/polyolefin copolymer is produced by reacting styrene (104.16 g, 1 mole) and butadiene (54.10 g, 1 mole) in the presence of 1 mole % 3-t-butoxy-propyllithium in an appropriate solvent (100 ml). The resulting copolymer is quenched with  
25 isopropyl alcohol (2 ml) and hydrogenated. The solvent is evaporated under reduced pressure. The residue (1.5 g) is taken up in tert-butylbenzene (25 ml) and Amberlyst® 15 ion exchange resin (1.5 g, ground powder, Aldrich) is added. The protecting group is removed by  
30 heating to reflux and monitoring the reaction by then layer chromatography (TLC) until complete. The product solution is filtered to remove the amberlyst resin. The solvent is evaporated under reduced pressure. The resulting copolymer is useful as a viscosity index  
35 improving additive for motor oils.

-48-

## EXAMPLE 8

## Preparation of

Poly(Alpha-Methylstyrene-Random-Isoprene) Copolymer

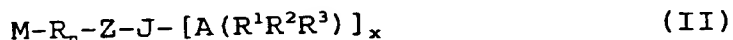
A polystyrene/polyolefin copolymer is  
5 produced by reacting alpha-methylstyrene (118.19 g, 1  
mole) and isoprene (68.13 g, 1 mole) in the presence of  
1 mole % 3-(t-butyldimethylsilyloxy)-1-propyllithium in  
an appropriate solvent (100 ml). The resulting  
copolymer is coupled with dimethyldichlorosilane (2 ml)  
10 and hydrogenated. The solvent is evaporated under  
reduced pressure. The residue (1.5 g) is taken up in  
tert-butylbenzene (25 ml) and Amberlyst® 15 ion  
exchanged resin (1.5 g, ground powder, Aldrich) is  
added. The protecting group is removed by heating to  
15 reflux and monitoring the reaction by thin layer  
chromatography (TLC) until complete. The product  
solution is filtered to remove the amberlyst resin.  
The solvent is evaporated under reduced pressure. The  
resulting copolymer is useful as a viscosity index  
20 improving additive for motor oils.

The foregoing examples are illustrative of  
the present invention and are not to be construed as  
limiting thereof. The invention is defined by the  
following claims, with equivalents of the claims to be  
25 included therein.

-49-

## THAT WHICH IS CLAIMED IS:

1. A copolymer produced by copolymerizing an alkenylsubstituted aromatic hydrocarbon and a conjugated diene, sequentially or in admixture, with a protected functional organometallic initiator of the  
5 formula



wherein:

M is an alkali metal;

R is a saturated or unsaturated hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated diene hydrocarbons, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof;

n is an integer from 0 to 5;

15 Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups;

A is an element selected from Group IVa of the Periodic Table of Elements;

20 J is oxygen, sulfur, or nitrogen;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, and cycloalkyl and substituted cycloalkyl containing 5 to 12 carbon atoms; and

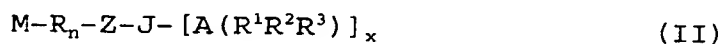
x is dependent on the valence of J and varies from one when J is oxygen or sulfur to two when J is  
30 nitrogen, to form a mono-protected, mono-functionalized living copolymer, followed by quenching or functionalizing the living copolymer with a functionalizing group to terminate and end-cap said living copolymer.

35 2. The copolymer of Claim 1, wherein said functionalizing compound is selected from the group

-50-

consisting of ethylene oxide, propylene oxide, styrene oxide, oxetane, oxygen, sulfur, carbon dioxide, chlorine, bromine, iodine, chlorotrimethylsilane, styrenyldimethyl chlorosilane, 1,3-propane sultone,  
 5 caprolactam, N-benzylidene trimethylsilylamide, dimethyl formamide, silicon acetals, 1,5-diazabicyclo[3.1.0]hexane, allyl bromide, allyl chloride, methacryloyl chloride, 3-(dimethylamino)-propyl chloride, N-(benzylidene)trimethylsilylamine,  
 10 epichlorohydrin, epibromohydrin, and epiiodohydrin.

3. A multi-branched or star-shaped copolymer having at least one functional end produced by copolymerizing an alkenylsubstituted aromatic hydrocarbon and a conjugated diene, sequentially or in  
 15 admixture, with a protected functional organolithium initiator having the formula:



wherein:

- M is an alkali metal;
- 20 R is a saturated or unsaturated hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated diene hydrocarbons, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof;
- 25 n is an integer from 0 to 5;
- Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups;
- A is an element selected from Group IVa of  
 30 the Periodic Table of Elements;
- J is oxygen, sulfur, or nitrogen;
- R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower  
 35 dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower

-51-

dialkylamino groups, and cycloalkyl and substituted cycloalkyl containing 5 to 12 carbon atoms; and

x is dependent on the valence of J and varies from one when J is oxygen or sulfur to two when J is nitrogen, to form a mono-protected, mono-functionalized living copolymer; and

coupling said living copolymer with at least one other living copolymer with a linking agent.

4. The copolymer of Claim 3, wherein said linking agent is selected from the group consisting of halosilanes, halostannanes, phosphorus halides, isomeric dialkenylaryls, isomeric divinylaryls, isomeric trivinylaryls, and mixtures thereof.

5. The copolymer of Claim 1 or 3, wherein said copolymer is produced by polymerizing said alkenylsubstituted aromatic hydrocarbon sequentially with said conjugated diene to form a block copolymer.

6. The copolymer of Claim 1 or 3, wherein said copolymer is produced by polymerizing a mixture of said alkenylsubstituted aromatic hydrocarbon and said conjugated diene in the presence of a polar modifier to form a random copolymer.

7. The copolymer of Claim 1 or 3, wherein said copolymer is produced by polymerizing a mixture of said alkenylsubstituted aromatic hydrocarbon and said conjugated diene to form a tapered copolymer.

8. The copolymer of Claim 1 or 3, wherein: said alkenylsubstituted aromatic hydrocarbon is selected from the group consisting of styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinylnaphthalene, 2-alpha-

-52-

5 methylvinyl-naphthalene, 1,2-diphenyl-4-methyl-1-hexene, alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl derivatives thereof in which the total number of carbon atoms in the combined hydrocarbon constituents is not greater than 18, and mixtures thereof; and

10 said conjugated diene is selected from the group consisting of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 15 and 2-methyl-3-isopropyl-1,3-butadiene.

9. The copolymer of Claim 8, wherein said alkenyl-substituted aromatic hydrocarbon is styrene and wherein said conjugated diene is 1,3-butadiene or isoprene.

20 10. The copolymer of Claim 1 or 3, wherein A is carbon or silicon.

11. The copolymer of Claim 1 or 3, wherein at least a portion of aliphatic unsaturation of said copolymer has been saturated with hydrogen.

25 12. The copolymer of Claim 11, wherein at least about 90% of aliphatic unsaturation has been saturated with hydrogen.

30 13. The copolymer of Claim 11, wherein at least a portion of aliphatic unsaturation of said copolymer has been saturated with hydrogen prior to deprotecting said copolymer.

-53-

14. The copolymer of Claim 11, wherein at least a portion of aliphatic unsaturation of said copolymer has been saturated with hydrogen after deprotecting said copolymer.

5           15. The copolymer of Claim 1 or 3, wherein  $[A(R^1R^2R^3)]_x$  has been removed.

16. The copolymer of Claim 1 or 3, wherein said organometallic initiator is selected from the group consisting of omega-(tert-alkoxy)-1-  
10 alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with  
15 conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, omega-(tert-butyldimethylsilyloxy)-1-alkyllithiums, omega-(tert-butyldimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-  
20 alkyllithiums chain-extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums.

17. The polymer of Claim 16, wherein said  
25 organometallic initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(tert-butyldimethylsilyloxy)-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(di-tert-butyldimethylsilylamino)-1-propyllithium, 3-(1,1-dimethylethoxy)-1-propyllithium,  
30 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-

- dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 3-(t-butyl dimethylsilyloxy)-1-propyllithium, 3-(t-butyl dimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyl dimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyl dimethylsilyloxy)-1-butyllithium, 5-(t-butyl dimethylsilyloxy)-1-pentyllithium, 6-(t-butyl dimethylsilyloxy)-1-hexyllithium, 8-(t-butyl dimethylsilyloxy)-1-octyllithium and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(dimethylamino)-2-methyl-1-propyllithium, 3-(dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(dimethylamino)-1-butyllithium, 5-(dimethylamino)-1-pentyllithium, 6-(dimethylamino)-1-hexyllithium, 8-(dimethylamino)-1-propyllithium, 4-(ethoxy)-1-butyllithium, 4-(propyloxy)-1-butyllithium, 4-(1-methylethoxy)-1-butyllithium, 3-(triphenylmethoxy)-2,2-dimethyl-1-propyllithium, 4-(triphenylmethoxy)-1-butyllithium, 3-[3-(dimethylamino)-1-propyloxy]-1-propyllithium, 3-[2-(dimethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diisopropyl)amino)-1-ethoxy]-1-propyllithium, 3-[2-(1-piperidino)-1-ethoxy]-1-propyllithium, 3-[2-(1-pyrrolidino)-1-ethoxy]-1-propyllithium, 4-[3-(dimethylamino)-1-propyloxy]-1-butyllithium, 6-[2-(1-piperidino)-1-ethoxy]-1-hexyllithium, 3-[2-(methoxy)-1-ethoxy]-1-propyllithium, 3-[2-(ethoxy)-1-ethoxy]-1-propyllithium, 4-[2-(methoxy)-1-ethoxy]-1-butyllithium, 5-[2-(ethoxy)-1-ethoxy]-1-pentyllithium, 3-[3-(methylthio)-1-propyloxy]-1-propyllithium, 3-[4-



-55-

- (methylthio)-1-butyloxy]-1-propyllithium, 3-(methylthiomethoxy)-1-propyllithium, 6-[3-(methylthio)-1-propyloxy]-1-hexyllithium, 3-[4-(methoxy)-benzyloxy]-1-propyllithium, 3-[4-(1,1-dimethylethoxy)-benzyloxy]-1-propyllithium, 3-[2,4-(dimethoxy)-benzyloxy]-1-propyllithium, 8-[4-(methoxy)-benzyloxy]-1-octyllithium, 4-[4-(methylthio)-benzyloxy]-1-butyllithium, 3-[4-(dimethylamino)-benzyloxy]-1-propyllithium, 6-[4-(dimethylamino)-benzyloxy]-1-hexyllithium, 5-(triphenylmethoxy)-1-pentyllithium, 6-(triphenylmethoxy)-1-hexyllithium, and 8-(triphenylmethoxy)-1-octyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-butyl dimethylsilylthio)-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-butyl dimethylsilylthio)-1-butyllithium, 6-(t-butyl dimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium, hydrocarbon soluble

-56-

conjugated alkadiene, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, chain extended oligomeric analogs thereof, and mixtures thereof.

18. The copolymer of Claim 1 or 3, wherein  
5 at least one functional group is deprotected, and wherein said copolymer further includes a di- or polyfunctional comonomer reacted with said at least one deprotected functional group, with the proviso that when J is reacted with said di- or polyfunctional  
10 comonomer, J is O or S.

19. The copolymer of Claim 18, wherein said comonomer is selected from the group consisting of diesters, polyesters, diisocyanates, polyisocyanates, diamides, polyamides, cyclic amides, dicarboxylic  
15 acids, polycarboxylic acids, diols, polyols and mixtures thereof.

20. The polymer of Claim 19, wherein said polymer includes at least one hydroxyl functional group, and wherein said at least one hydroxyl  
20 functional group is reacted with diisocyanate and diol to produce polyurethane blocks.

21. The polymer of Claim 20, wherein said diol includes acid group functionalities, and wherein said acid group functionalities are neutralized with  
25 tertiary amines to provide dispersibility in water.

22. The polymer of Claim 19, wherein said polymer includes at least one hydroxyl functional group, and wherein said at least one hydroxyl  
functional group is reacted with diacid or anhydride  
30 and diamine or lactam to produce polyamide blocks.

-57-

23. The polymer of Claim 19, wherein said polymer includes at least one hydroxyl functional group, and wherein said at least one hydroxyl functional group is reacted with diacid or anhydride  
5 and diol or polyol to produce polyester blocks.

24. The polymer of Claim 23, wherein at least a portion of said diacid or anhydride is substituted by an unsaturated acid or anhydride to provide unsaturated polyester blocks capable of  
10 crosslinking with unsaturated monomers by addition of free radical initiators.

25. The polymer of Claim 19, wherein said polymer includes at least one hydroxyl functional group, and wherein said at least one hydroxyl  
15 functional group is reacted with anhydride to form a half-ester with free carboxyl functionality at the terminus thereof.

26. The polymer of Claim 25, wherein said carboxyl functional terminal groups are further reacted  
20 with epoxy resins and amine curing agents to form epoxy resin composites.

27. The polymer of Claim 19, wherein said polymer includes at least one hydroxyl functional group, and wherein said at least one hydroxyl  
25 functional group is reacted with methacroyl chloride to provide polymerizable alkenyl groups at the terminus thereof.

28. The polymer of Claim 27, further comprising acrylic monomers polymerized by use of free  
30 radical initiators onto said alkenyl terminal groups.

-58-

29. The polymer of Claim 28, wherein said acrylic acid monomers are functional or amide functional acrylic monomers to provide polar hydrophilic polymer segments.

5           30. The polymer of Claim 27, wherein sulfonated styrene and/or 4-vinyl pyridine are polymerized by free radical initiators onto said terminal alkenyl groups to provide functional polymer segments capable of improving dispersability of the  
10 polymer.

          31. The polymer of Claim 19, wherein said polymer includes at least one hydroxyl functional group, and wherein said at least one hydroxyl functional group is reacted with sulfonyl chloride in  
15 the presence of a tertiary amine catalyst to form sulfonate functional groups at the terminus thereof.

          32. The polymer of Claim 31, wherein said sulfonate functional groups are reacted with primary amines or ammonia, under heat and pressure, to form  
20 polymers with amine functionality at the terminus thereof.

          33. The polymer of Claim 25, wherein said carboxyl functional groups are reacted with an epoxy resin and an excess of amine to completely react all of  
25 the epoxy groups, the excess amine is removed by distillation, and the resulting epoxy-amine adduct is reacted with a water soluble organic or inorganic acid to form water soluble quarternary ammonium containing polymers.

30           34. The copolymer of Claim 3, wherein said copolymer includes at least one functional end and at least one non-functional end prepared by copolymerizing

-59-

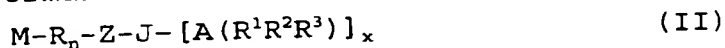
an alkenylsubstituted aromatic hydrocarbon and a  
conjugated diene, sequentially or in admixture, with  
said protected functional organolithium initiator of  
Formula (II) and in addition with a non-functional  
5 organometallic initiator.

35. The copolymer of Claim 3, wherein said  
copolymer includes at least two functional ends having  
different functional groups prepared by copolymerizing  
an alkenylsubstituted aromatic hydrocarbon and a  
10 conjugated diene, sequentially or in admixture, with  
protected functional organolithium initiators of  
Formula (II) in which J is different.

36. The copolymer of Claim 3, wherein said  
copolymer includes at least two functional ends having  
15 different protecting groups prepared by copolymerizing  
an alkenylsubstituted aromatic hydrocarbon and a  
conjugated diene, sequentially or in admixture, with  
protected functional organolithium initiators of  
Formula (II) in which  $[A(R^1R^2R^3)]_x$  is different.

20 37. A process for preparing copolymers,  
comprising:

copolymerizing an alkenylsubstituted aromatic  
hydrocarbon and a conjugated diene, sequentially or in  
admixture, with a protected functional organometallic  
25 initiator of the formula



wherein:

M is an alkali metal;

R is a saturated or unsaturated hydrocarbyl  
30 group derived by incorporation of a compound selected  
from the group consisting of conjugated diene  
hydrocarbons, alkenylsubstituted aromatic hydrocarbons,  
and mixtures thereof;

n is an integer from 0 to 5;

-60-

Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups;

A is an element selected from Group IVa of  
5 the Periodic Table of Elements;

J is oxygen, sulfur, or nitrogen;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower  
10 dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, and cycloalkyl and substituted cycloalkyl containing 5 to 12 carbon atoms; and

x is dependent on the valence of J and varies  
15 from one when J is oxygen or sulfur to two when J is nitrogen, to form a mono-protected, mono-functionalized living polymer.

38. The process of Claim 37, further comprising quenching said living copolymer after said  
20 copolymerizing step.

39. The process of Claim 37, further comprising functionalizing said living copolymer with a functionalizing compound capable of terminating and end-capping said living copolymer after said  
25 copolymerizing step.

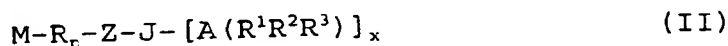
40. The process of Claim 37, wherein said functionalizing step comprises functionalizing said living copolymer with a functionalizing compound selected from the group consisting of ethylene oxide,  
30 propylene oxide, styrene oxide, oxetane, oxygen, sulfur, carbon dioxide, chlorine, bromine, iodine, chlorotrimethylsilane, styrenyldimethyl chlorosilane, 1,3-propane sultone, caprolactam, N-benzylidene trimethylsilylamide, dimethyl formamide, silicon

-61-

acetals, 1,5-diazabicyclo[3.1.0]hexane, allyl bromide, allyl chloride, methacryloyl chloride, 3-(dimethylamino)-propyl chloride, N-(benzylidene)trimethylsilylamine, epichlorohydrin, epibromohydrin, and epiodohydrin.

41. A process for preparing a multi-branched or star-shaped polymer, comprising:

copolymerizing an alkenylsubstituted aromatic hydrocarbon and a conjugated diene, sequentially or in admixture, with a protected functional organometallic initiator of the formula



wherein:

M is an alkali metal;

R is a saturated or unsaturated hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated diene hydrocarbons, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof;

n is an integer from 0 to 5;

Z is a branched or straight chain hydrocarbon group which contains 3-25 carbon atoms, optionally containing aryl or substituted aryl groups;

J is oxygen, sulfur, or nitrogen;

A is an element selected from Group IVa of the Periodic Table of Elements;

$R^1$ ,  $R^2$ , and  $R^3$  are independently selected from hydrogen, alkyl, substituted alkyl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, aryl or substituted aryl groups containing lower alkyl, lower alkylthio, and lower dialkylamino groups, and cycloalkyl and substituted cycloalkyl containing 5 to 12 carbon atoms; and

x is dependent on the valence of J and varies from one when J is oxygen or sulfur to two when J is nitrogen, to form a mono-protected, mono-functionalized living polymer; and

-62-

coupling said living polymer with at least one other living polymer with a linking agent.

42. The process of Claim 41, wherein said linking agent is selected from the group consisting of  
5 halosilanes, halostannes, phosphorus halides, isomeric dialkenylaryls, isomeric divinylaryls, isomeric trivinylaryls, and mixtures thereof.

43. The process of Claim 37 or 41, wherein said copolymerizing step comprises copolymerizing said  
10 alkenylsubstituted aromatic hydrocarbon sequentially with said conjugated diene to form a block copolymer.

44. The process of Claim 37 or 41, wherein said copolymerizing step comprises copolymerizing a mixture of said alkenylsubstituted aromatic hydrocarbon  
15 and said conjugated diene in the presence of a polar modifier to form a random copolymer.

45. The process of Claim 37 or 41, wherein said copolymerizing step comprises copolymerizing a mixture of said alkenylsubstituted aromatic hydrocarbon  
20 and said conjugated diene to form a tapered copolymer.

46. The process of Claim 37 or 41, wherein:  
said alkenylsubstituted aromatic hydrocarbon is selected from the group consisting of styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-  
25 vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinylnaphthalene, 2-alpha-methylvinylnaphthalene, 1,2-diphenyl-4-methyl-1-hexene, alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl derivatives thereof in which the total number of carbon  
30 atoms in the combined hydrocarbon constituents is not greater than 18, and mixtures thereof; and



-63-

said conjugated diene is selected from the group consisting of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, and 2-methyl-3-isopropyl-1,3-butadiene.

47. The process of Claim 46, wherein said alkenylsubstituted aromatic hydrocarbon is styrene and wherein said conjugated diene is 1,3-butadiene or isoprene.

48. The process of Claim 37 or 41, wherein A is carbon or silicon.

49. The process of Claim 37 or 41, further comprising after said copolymerizing step the step of saturating at least a portion of aliphatic unsaturation of said copolymer with hydrogen.

50. The process of Claim 49, wherein said saturating step comprises saturating at least about 90% of the aliphatic unsaturation with hydrogen.

51. The process of Claim 49, wherein said saturating step comprises saturating said copolymer prior to deprotecting said copolymer.

52. The process of Claim 49, further comprising deprotecting said copolymer prior to said saturating step.

-64-

53. The process of Claim 37 or 41, further comprising deprotecting said copolymer.

54. The process of Claim 37 or 41, wherein said organometallic initiator is selected from the group consisting of omega-(tert-alkoxy)-1-alkyllithiums, omega-(tert-alkoxy)-1-alkyllithiums chain extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, omega-(tert-alkylthio)-1-alkyllithiums, omega-(tert-alkylthio)-1-alkyllithiums chain extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, omega-(tert-butyldimethylsilyloxy)-1-alkyllithiums, omega-(tert-butyldimethylsilylthio)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums, omega-(dialkylamino)-1-alkyllithiums chain-extended with conjugated alkadienes, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, and omega-(bis-tert-alkylsilylamino)-1-alkyllithiums.

55. The process of Claim 54, wherein said organometallic initiator is selected from the group consisting of 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(tert-butyldimethylsilyloxy)-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(dimethylamino)-1-propyllithium, 3-(di-tert-butyldimethylsilylamino)-1-propyllithium, 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropoxy)-1-butyllithium,

-65-

- 5- (1,1-dimethylpropoxy)-1-pentyllithium, 6- (1,1-dimethylpropoxy)-1-hexyllithium, 8- (1,1-dimethylpropoxy)-1-octyllithium, 3- (t-butylldimethylsilyloxy)-1-propyllithium, 3- (t-butylldimethylsilyloxy)-2-methyl-1-propyllithium, 3- (t-butylldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4- (t-butylldimethylsilyloxy)-1-butyllithium, 5- (t-butylldimethylsilyloxy)-1-pentyllithium, 6- (t-butylldimethylsilyloxy)-1-hexyllithium, 8- (t-butylldimethylsilyloxy)-1-octyllithium and 3- (trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3- (dimethylamino)-1-propyllithium, 3- (dimethylamino)-2-methyl-1-propyllithium, 3- (dimethylamino)-2,2-dimethyl-1-propyllithium, 4- (dimethylamino)-1-butyllithium, 5- (dimethylamino)-1-pentyllithium, 6- (dimethylamino)-1-hexyllithium, 8- (dimethylamino)-1-propyllithium, 4- (ethoxy)-1-butyllithium, 4- (propyloxy)-1-butyllithium, 4- (1-methylethoxy)-1-butyllithium, 3- (triphenylmethoxy)-2,2-dimethyl-1-propyllithium, 4- (triphenylmethoxy)-1-butyllithium, 3- [3- (dimethylamino)-1-propyloxy]-1-propyllithium, 3- [2- (dimethylamino)-1-ethoxy]-1-propyllithium, 3- [2- (diethylamino)-1-ethoxy]-1-propyllithium, 3- [2- (diisopropyl)amino)-1-ethoxy]-1-propyllithium, 3- [2- (1-piperidino)-1-ethoxy]-1-propyllithium, 3- [2- (1-pyrrolidino)-1-ethoxy]-1-propyllithium, 4- [3- (dimethylamino)-1-propyloxy]-1-butyllithium, 6- [2- (1-piperidino)-1-ethoxy]-1-hexyllithium, 3- [2- (methoxy)-1-ethoxy]-1-propyllithium, 3- [2- (ethoxy)-1-ethoxy]-1-propyllithium, 4- [2- (methoxy)-1-ethoxy]-1-butyllithium, 5- [2- (ethoxy)-1-ethoxy]-1-pentyllithium, 3- [3- (methylthio)-1-propyloxy]-1-propyllithium, 3- [4- (methylthio)-1-butyloxy]-1-propyllithium, 3- (methylthiomethoxy)-1-propyllithium, 6- [3- (methylthio)-1-propyloxy]-1-hexyllithium, 3- [4- (methoxy)-benzyloxy]-1-propyllithium, 3- [4- (1,1-dimethylethoxy)-benzyloxy]-1-propyllithium, 3- [2,4- (dimethoxy)-benzyloxy]-1-

- 66 -

- propyllithium, 8-[4-(methoxy)-benzyloxy]-1-octyllithium, 4-[4-(methylthio)-benzyloxy]-1-butyllithium, 3-[4-(dimethylamino)-benzyloxy]-1-propyllithium, 6-[4-(dimethylamino)-benzyloxy]-1-hexyllithium, 5-(triphenylmethoxy)-1-pentyllithium, 6-(triphenylmethoxy)-1-hexyllithium, and 8-(triphenylmethoxy)-1-octyllithium, 3-(hexamethyleneimino)-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 8-(hexamethyleneimino)-1-octyllithium, 3-(t-butyldimethylsilylthio)-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilylthio)-1-butyllithium, 6-(t-butyldimethylsilylthio)-1-hexyllithium, 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, and 8-(1,1-dimethylpropylthio)-1-octyllithium, hydrocarbon soluble conjugated alkadiene, alkenylsubstituted aromatic hydrocarbons, and mixtures thereof, chain extended oligomeric analogs thereof, and mixtures thereof.

-67-

56. The process of Claim 37 or 41, further comprising copolymerizing said copolymer with at least one di- or polyfunctional comonomer.

57. The process of Claim 56, wherein said  
5 comonomer is selected from the group consisting of diesters, polyesters, diisocyanates, polyisocyanates, diamides, polyamides, cyclic amides, dicarboxylic acids, polycarboxylic acids, diols, polyols and mixtures thereof.

10 58. The process of Claim 41, wherein said polymerizing step comprises polymerizing an alkenylsubstituted aromatic hydrocarbon and a conjugated diene, sequentially or in admixture, with at least one protected functional organometallic initiator  
15 of Formula (II) and at least one non-functional organometallic initiator to provide a multi-branched or star-shaped polymer having at least one functional end and at least one non-functional end.

59. The process of Claim 41, wherein said  
20 polymerizing step comprises polymerizing an alkenylsubstituted aromatic hydrocarbon and a conjugated diene, sequentially or in admixture, with at least two protected functional organometallic  
initiators of Formula (II) in which J is different to  
25 provide a multi-branched or star-shaped polymer having at least two different functional ends.

60. The process of Claim 41, wherein said  
polymerizing step comprises polymerizing an  
alkenylsubstituted aromatic hydrocarbon and a  
30 conjugated diene, sequentially or in admixture, with at least two protected functional organometallic  
initiators of Formula (II) in which  $[A(R^1R^2R^3)]_x$  is different to provide a multi-branched or star-shaped

-68-

polymer having at least two different protecting groups.

61. A process for modifying the surface adhesion properties of polyolefins, comprising melt  
5 mixing the functional polymer of Claim 1 or 3 with a polyolefin in an amount of 1 to 25% by weight based on the polyolefin.

62. The process of Claim 61, wherein the polyolefin is selected from the group consisting of low  
10 density polyethylene, linear low density polyethylene, high density polyethylene, polypropylene, polyisobutylene, and copolymers and blends thereof.

63. A polymer produced by reacting a living copolymer of Claim 1 with a difunctional linking agent  
15 to produce a telechelic, di-protected, di-functional copolymer.

64. The polymer of Claim 63, wherein the difunctional linking agent is selected from the group consisting of ethylbenzoate, xylene dibromide, and  
20 dichlorodimethylsilane.

65. The polymer of Claim 63, wherein the living copolymer before linking is a sequential or tapered diblock copolymer with protected functionality at the initiating chain ends thereof and the polymer  
25 after linking is a triblock copolymer with telechelic protected functionalities.

66. The polymer of Claim 63, wherein the living copolymer before linking is a sequential or tapered diblock copolymer, and the polymer after  
30 linking is a telechelic di-protected, di-functional triblock copolymer.

-69-

67. The polymer of Claim 66, wherein the di-protected, di-functional triblock copolymer is deprotected.

5 68. The polymer of Claim 67, wherein the deprotected polymer is a telechelic polymer having dihydroxyl functionality.

69. The polymer of Claim 67, wherein said deprotected di-functional triblock copolymer is copolymerized with a comonomer or comonomers selected  
10 from the group consisting of diesters, polyesters, diisocyanates, polyisocyanates, diamides, polyamides, cyclic amides, dicarboxylic acids, polycarboxylic acids, diols, polyols, and mixtures thereof.

70. A process for preparing a telechelic,  
15 di-protected, di-functional copolymer, comprising reacting a living copolymer of Claim 1 with a difunctional linking agent to produce a telechelic, di-protected, di-functional copolymer.

71. The process of Claim 70, wherein the  
20 difunctional linking agent is selected from the group consisting of ethylbenzoate, xylene dibromide, and dichlorodimethylsilane.

72. The process of Claim 70, wherein the  
25 living copolymer before linking is a sequential or tapered diblock copolymer with protected functionality at the initiating chain ends thereof and the polymer after linking is a triblock copolymer with telechelic protected functionalities.

73. The process of Claim 70, wherein the  
30 living copolymer before linking is a sequential or tapered diblock copolymer, and the polymer after

-70-

linking is a telechelic di-protected, di-functional triblock copolymer.

74. The process of Claim 73, further comprising deprotecting the di-protected, di-functional  
5 triblock copolymer.

75. The process of Claim 74, wherein the deprotected copolymer is a telechelic di-hydroxyl functional polymer.

76. The polymer of Claim 74, further  
10 comprising copolymerizing said deprotected di-functional triblock copolymer with a comonomer or comonomers selected from the group consisting of diesters, polyesters, diisocyanates, polyisocyanates, diamides, polyamides, cyclic amides, dicarboxylic  
15 acids, polycarboxylic acids, diols, polyols, and mixtures thereof.



# INTERNATIONAL SEARCH REPORT

Interns 1 Application No  
PCT/US 96/12519

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F236/10 C08F297/04 C08C19/44 C08F8/00 C08F4/46  
C08F4/72

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 241 239 (SECR DEFENCE) 28 August 1991 cited in the application see page 4, line 10 - line 33; claims 1,7,22-26 see page 6, line 18 - page 7, line 22 ---	1-10, 37-48, 54,55
P,X	WO,A,95 22566 (FMC CORP) 24 August 1995 see page 8, line 10 - line 16; claims 6-30 ---	1-18, 37-56
P,X	US,A,5 527 753 (ENGEL JOHN F ET AL) 18 June 1996 see column 4, line 63 - column 5, line 35; claim 1 see column 6, line 8 - line 16 -----	1-17, 37-55

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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